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13. ABSTRACT (Maximum 200 Words)

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The processing, properties, and performance of zirconium diboride ceramics were studied. The initial phase of the work focused on improving the properties of zirconium diboride-silicon carbide ceramics prepared from commercial powders by minimizing the impurity content and controlling the grain size of ceramics prepared by conventional hot pressing. Strengths of more than 1000 MPa (1 GPa) were measured for zirconium diboride containing 20 or 30 volume percent silicon carbide, much higher than previous reports. Another aspect of the work focused on controlling the meso-scale architecture of zirconium diboride based ceramics using co-extrusion processing. The resulting fibrous monolithic ceramics demonstrated non-catastrophic failure behavior. As part of this research, a pressureless sintering process was developed whereby zirconium diboride could be sintered to near theoretical density without applied pressure or liquid phase sintering aids. Development of the sintering process continues under follow-on funding through the Air Force Research Laboratory. The oxidation behavior of zirconium diboride ceramics was examined in static oxidation testing and arc jet testing. Finally, reactive processes were developed to produce zirconium diboride and zirconium diboride-silicon carbide ceramics.

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TABLE OF CONTENTS

EXECUTIVE SUMMARY.....	4
OBJECTIVES.....	5
STATUS OF EFFORT	5
ACCOMPLISHMENTS/NEW FINDINGS.....	5
CONVENTIONAL PROCESSING.....	5
CO-EXTRUSION FORMING	10
PRESSURELESS DENSIFICATION	13
OXIDATION	14
REACTIVE PROCESSING.....	15
SUMMARY AND IMPACT	18
PERSONNEL SUPPORTED	20
PUBLICATIONS AND PRESENTATIONS.....	20
PEER-REVIEWED PUBLICATIONS	20
THESIS/DISSERTATION	20
INVITED PRESENTATIONS	21
CONTRIBUTED PRESENTATIONS.....	21
POSTERS.....	22
NEWSPAPERS.....	22
RADIO.....	23
TELEVISION.....	23
PROFESSIONAL/TECHNICAL PUBLICATIONS	23
INTERACTIONS/TRANSITIONS.....	23
NEW DISCOVERIES, INVENTIONS, AND PATENT DISCLOSURES	24
HONORS/AWARDS	24
AWARDS FOR DR. FAHRENHOLTZ.....	24
AWARDS FOR DR. HILMAS.....	25
AWARDS FOR ADAM CHAMBERLAIN.....	25
AWARDS FOR MICHELLE SCHAEFFLER.....	25
APPENDIX A. SUMMARY OF INTERACTIONS WITH ISTE.....	26
APPENDIX B. DISSERTATION OF ADAM CHAMBERLAIN.....	31
APPENDIX C. DISSERTATION OF JIM ZIMMERMANN.....	32
APPENDIX D. PUBLICATIONS.....	33
LIST OF PUBLICATIONS	33
COVER PHOTOGRAPH.....	33
SUBMITTED MANUSCRIPT	33

LIST OF FIGURES

Figure 1.	A polished, thermally etched cross section of ZrB_2 hot pressed at 1900°C	7
Figure 2.	SEM micrographs of (a) polished and (b) polished, thermally etched cross section of ZrB_2 -30% SiC hot pressed at 1900°C	8
Figure 3.	SEM micrographs of (a) polished and (b) polished, thermally etched cross section of ZrB_2 -30% MoSi_2 hot pressed at 1900°C	8
Figure 4.	Polished, thermally etched cross sections of ZrB_2 -30 vol.% SiC prepared from powders that were milled with (a) WC, (b), ZrO_2 , and (c) SiC milling media.	9
Figure 5.	A large SiC agglomerate characteristic of defects in ZrB_2 -30 vol.% SiC prepared from powders that were milled with SiC milling media.	9
Figure 6.	A schematic illustration of the typical fibrous monolithic architecture produced by co-extrusion. The gray material represents the strong, hard cells, while the black represents the cell boundaries.	10
Figure 7.	A fibrous monolith architecture consisting of dense ZrB_2 -SiC cells and porous ZrB_2 cell boundaries prepared by two-pass co-extrusion.	11
Figure 8.	He and Hutchinson analysis of the relative fracture energy of the cell and cell boundary as a function of the relative modulus values of the cells and cell boundaries (Dunder's α) showing that crack deflection should occur when the carbon content of ZrB_2 -carbon cell boundaries is 85 vol.% or greater.	12
Figure 9.	A fibrous monolith architecture consisting of dense ZrB_2 -SiC cells and ZrB_2 -carbon cell boundaries prepared by single-pass co-extrusion.	12
Figure 10.	Fracture surfaces of FMs with ZrB_2 -SiC cells and ZrB_2 -carbon cell boundaries containing 30, 40, and 50 vol.% amorphous carbon.	12
Figure 11.	(a) A load-deflection curve and (b) a picture of a fractured specimen of a FM demonstrating non-catastrophic failure.	13
Figure 12.	Relative density of ZrB_2 sintered in argon as (a) a function of temperature and (b) a function of hold time at 2150°C	14
Figure 13.	Micrographs of (a) polished and (b) thermally etched cross sections of ZrB_2 densified by pressureless sintering at 2150°C	14
Figure 14.	A volatility diagram for the combined ZrB_2 and SiC system showing the vapor pressure of the predominant gaseous species as a function of oxygen partial pressure at 1500°C	15
Figure 15.	A schematic illustration of the layered structure that develops on the surface of ZrB_2 -SiC during oxidation at 1500°C in air. The diagram shows the oxygen partial pressures and the relative motion of the interfaces.	16
Figure 16.	Cross sections of ZrB_2 produced by reactive hot pressing at (a) 1900°C and (b) 2050°C	17

LIST OF TABLES

Table I.	Temperature, time, pressure profile used for hot pressing $\text{ZrB}_2\text{-SiC}$.	6
Table II.	Physical and mechanical properties of $\text{ZrB}_2\text{-SiC}$ materials.	6
Table III.	Physical and mechanical properties of $\text{ZrB}_2\text{-MoSi}_2$ materials.	7
Table IV.	Physical and mechanical properties of $\text{ZrB}_2\text{-SiC}$ materials prepared from precursor powders that were attrition milled using different milling media.	9
Table V.	Heating schedule for reactively hot pressed ZrB_2 ceramics.	17
Table VI.	Physical and mechanical properties of ZrB_2 prepared by reactive hot pressing compared to conventional hot pressing.	18
Table VII.	The physical and mechanical properties of $\text{ZrB}_2\text{-30% SiC}$ prepared by reactive hot pressing (RHP) compared to conventional hot pressing (HP).	18
Table VIII.	Personnel supported during this project.	20

EXECUTIVE SUMMARY

This report summarizes the technical progress and potential impact of research performed as part of the project "Reactive Processing and Co-Extrusion of Ultra-High Temperature Ceramics and Composites" that was funded by AFOSR grant F-49620-03-1-0072. The report lists all of the publications and presentations that stemmed from the project. In addition, the report summarizes interactions between the project team and other members of the ultra-high temperature ceramic community including the NASA-Ames Research Center, the Air Force Research Laboratory, the High Temperature Materials Group at Boeing-St. Louis, and the Institute for the Science and Technology of Ceramics (ISTEC) in Faenza, Italy.

Ultra-high temperature ceramics (UHTCs) are a unique class of materials with melting temperatures in excess of 3000°C. The borides, carbides, and nitrides of the early transition metals (Zr, Hf, Ta, etc.) are UHTCs. In addition to high melting temperatures, these ceramics are promising candidates for applications that involve extreme temperatures and/or chemically aggressive environments such as those associated with hypersonic flight, atmospheric re-entry, and rocket propulsion. Improved UHTCs are needed to address future military needs related to global reach, time-to-target, and extending the vertical limit of the battlefield. In addition, UHTCs are a potential solution for dual use applications related to low cost access to space.

The project goal was to produce UHTCs with improved performance for thermal protection applications. Zirconium diboride (ZrB_2) and its composites with silicon carbide (SiC) and molybdenum disilicide (MoSi_2) were examined. Two main approaches were pursued: 1) the use of reactive processing; and 2) the control of structure at the meso-scale using co-extrusion processing. Significant technical progress was made in several areas.

The processing of UHTCs was studied. Initially, the effort used commercially available powders to produce ZrB_2 - SiC . By controlling the final grain size and minimizing impurity content, ZrB_2 -based ceramics with strengths over 1000 MPa (1 GPa) were produced for the first time. This initial processing research also led to the development of a pressureless sintering process to produce ZrB_2 with a relative density of more than 98% without the use of applied pressure or the addition of liquid phase sintering aids. The final year of the project focused on the development of reaction-based processes for the fabrication of ZrB_2 and ZrB_2 - SiC . The reaction of Zr and B was studied to investigate fundamental aspects of the formation of ZrB_2 . The knowledge gained was then applied to produce ZrB_2 - SiC . Dense ZrB_2 - SiC with high strength (~800 MPa) was produced at temperatures as low as 1650°C using reactive hot pressing.

The other major aspect of the project was the development of co-extrusion processes for the fabrication of ZrB_2 based fibrous monolithic materials. As part of this effort, processing methodologies were investigated to produce materials that combined the high strength ZrB_2 - SiC cells with UHTC cell boundaries to manipulate the fracture behavior and thermal shock performance. Modeling revealed that the strength of the cell boundaries relative to the ZrB_2 - SiC cells was a critical factor determining whether fibrous monolithic materials demonstrated brittle failure, like typical ceramics, or if a significant fraction of the failure load could be supported after an initial failure event. The project demonstrated non-catastrophic failure behavior in ZrB_2 -based fibrous monoliths that incorporated cell boundaries containing carbon and ZrB_2 .

Finally, fundamental oxidation behavior of ZrB_2 - SiC was investigated. A ZrB_2 volatility diagram was combined with a volatility diagram for SiC to understand the development of a SiC -depleted region during oxidation of ZrB_2 - SiC at 1500°C in air. This research may eventually lead to the production of UHTCs with improved oxidation resistance.

OBJECTIVES

The goal of this project was to produce ultra-high temperature ceramics (UHTCs) with improved performance for thermal protection applications. The two main approaches that were investigated were the reaction-based processing of conventional $\text{ZrB}_2\text{-SiC}$ ceramics and the co-extrusion fabrication of ZrB_2 -based fibrous monolithic materials. As part of this research, fundamental aspects of the processing, microstructure development, properties, and performance of zirconium diboride-based ceramics were investigated. Significant progress was achieved in several areas including:

1. Producing ZrB_2 -based ceramics with improved strength
2. Controlling the meso-scale architecture of ultra-high temperature ceramics using co-extrusion processing
3. Densification of ZrB_2 by conventional pressureless sintering
4. Understanding the oxidation mechanisms of ZrB_2 and $\text{ZrB}_2\text{-SiC}$
5. Developing reaction-based processing methods to produce ZrB_2 -based ceramics

STATUS OF EFFORT

This program began in January 2003 and was completed in December 2005. Significant progress was made toward the research objectives. This program is expected to have lasting impacts in several areas. First, the research led to the highest strengths reported to date for zirconium diboride based ceramics. Second, co-extrusion processing methods were developed to control the meso-scale structure of ZrB_2 -based ceramics. A pressureless sintering process was developed for ZrB_2 . In addition, a fundamental understanding of the oxidation of ZrB_2 and $\text{ZrB}_2\text{-SiC}$ was explored. Finally, reactive processes were investigated to produce higher purity, finer grain size ZrB_2 -based ceramics. The relevant historic and current technical literature related to UHTCs is reviewed in the publications that resulted from this work and is not further reviewed in this document.

In addition to the technical progress, this project served as the cornerstone for the growth of a broad research effort in ultra-high temperature ceramics at the University of Missouri-Rolla. This AFOSR grant provided the initial funding for UHTC research at UMR. The UHTC effort at UMR has now expanded to include related projects sponsored by the National Science Foundation, the U.S. Army Space and Missile Defense command, the Air Force Research Laboratory, Advanced Ceramics Research, Inc., the Naval Surface Warfare Center-Cardero Division, and the Defense University Research Instrumentation Program.

ACCOMPLISHMENTS/NEW FINDINGS

The beginning of this project coincided with a resurgence of interest in UHTCs based on military and civilian needs related to hypersonic flight and reusable atmospheric re-entry vehicles. Fundamental research on the processing and properties of UHTCs had been dormant since previous studies, many funded by the Air Force, were conducted in the 1950s, 60s and 70s. Subsequent increases in the purity and decreases in starting particle size of the starting materials combined with general improvements in processing and characterization methods created a need to define a "state-of-the-art." The conventional processing section represents this "state-of-the-art" study, while the other focus areas represent new approaches to improve UHTC performance.

Conventional Processing

The initial phase of the work focused on preparing dense ZrB_2 -based ceramics from commercially available precursor powders. Because pure ZrB_2 has poor resistance to oxidation,

additives were pursued as method to improve the oxidation resistance. Standard ceramic processing techniques and characterization methods were used in this study.

Zirconium diboride (Grade B, H.C. Starck) was combined with one of two different additives, SiC (UF-10, H.C. Starck) or MoSi₂ (Grade B, H.C. Starck), in this phase of the work. The amounts of the additives were varied from 0 to 30 volume percent. Powders were mixed by attrition milling for two hours in hexane using WC milling media. After milling, powders were dried using rotary evaporation to minimize segregation during drying, which can be driven by density differences between the constituents. Powders were consolidated by hot pressing. Graphite dies were lined with graphite foil and then coated with BN. The ramp rates, hold times, atmosphere, and load applied to the specimen for densification are summarized in Table I.

Table I. Temperature, time, pressure profile used for hot pressing ZrB₂-SiC.

Temperature Range (°C)	Ramp (°C/min)	Hold time (min)	Atmosphere	Load (MPa)
RT-1450	20	120	Vacuum	-
1450-1650	20	60	Vacuum	-
1650-1900	10	45	Argon	-
1900-1750	20	-	Argon	32
1750-RT	Furnace rate		Argon	-

After densification, the bulk density of hot pressed billets was measured by the Archimedes' method. Because of the incorporation of an unknown amount of WC into the powders during the milling process and unknown chemical processes during densification, the true density of each composition was measured using helium pycnometry. In turn, bulk density was divided by true density to calculate the percent theoretical density. Density data for ZrB₂-SiC are summarized in Table II while data from ZrB₂-MoSi₂ are given in Table III.

Table II. Physical and mechanical properties of ZrB₂-SiC materials.

SiC Content (Vol.%)	Relative Density (%)	Young's Modulus (GPa)	Hardness (GPa)	Strength (MPa)	Toughness (MPa•m ^{1/2})
0	99	489	23	565	3.5
10	93	450	24	713	4.1
20	99	466	24	1003	4.4
30	99	484	24	1089	5.3

The microstructures of the various materials were characterized using scanning electron microscopy. Polished, thermally etched sections of monolithic ZrB₂ (Figure 1) showed that the material had a high relative density (very little apparent porosity) and that the grain size was ~6 μm. A lighter phase was also observed in the sections. This is a W containing phase that is a result of WC impurities introduced during attrition milling. Additions of SiC (Figure 2) and MoSi₂ (Figure 3) were shown to decrease the grain size without adversely affecting density. In

both cases, the additives were well distributed within the matrix. Phases containing W were also observed in these materials, although they were more obvious on the polished sections.

Table III. Physical and mechanical properties of ZrB_2 - MoSi_2 materials.

MoSi ₂ Content (Vol.%)	Relative Density (%)	Young's Modulus (GPa)	Hardness (GPa)	Strength (MPa)	Toughness (MPa·m ^{1/2})
0	99	489	23	565	3.5
10	98	516	20	1151	4.1
20	98	523	19	1008	3.0
30	99	494	18	1031	4.0

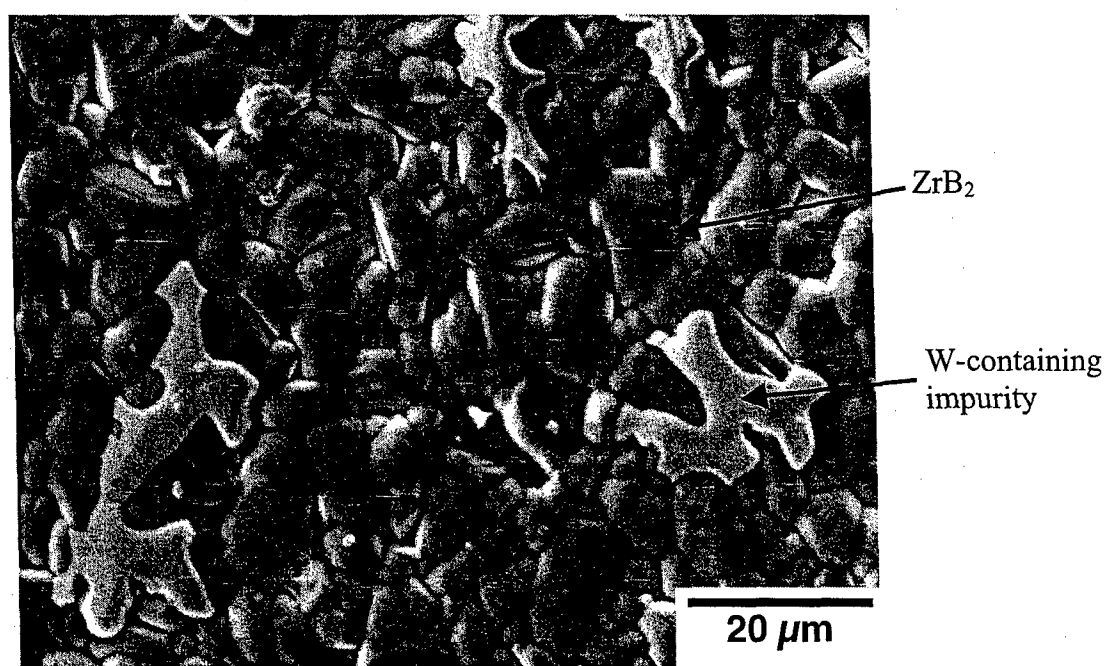


Figure 1. A polished, thermally etched cross section of ZrB_2 hot pressed at 1900°C.

The physical and mechanical properties of the materials were characterized. Young's modulus was determined according to ASTM C1259 (impulse excitation). Hardness was measured using Vickers' indentation with a 1 kg load and a 30 s dwell time. Strength was measured in four point bending according to ASTM C1161 for size A bend bars. At least ten bars were fractured to determine the reported strengths. Finally, fracture toughness was measured by fracturing size A bars with radial-median cracks produced by indentation with a 20 kg load according to the method of Chantikul.¹ Mechanical property data are tabulated for ZrB_2 -SiC compositions in Table II and ZrB_2 - MoSi_2 compositions in Table III.

¹ P. Chantikul, G.R. Anstis, B.R. Lawn, and D.B. Marshall, "A Critical Evaluation of Indentation techniques for Measuring Fracture Toughness: II. Strength Method," J. Am. Ceram. Soc., 64(9) 539-543 (1981).

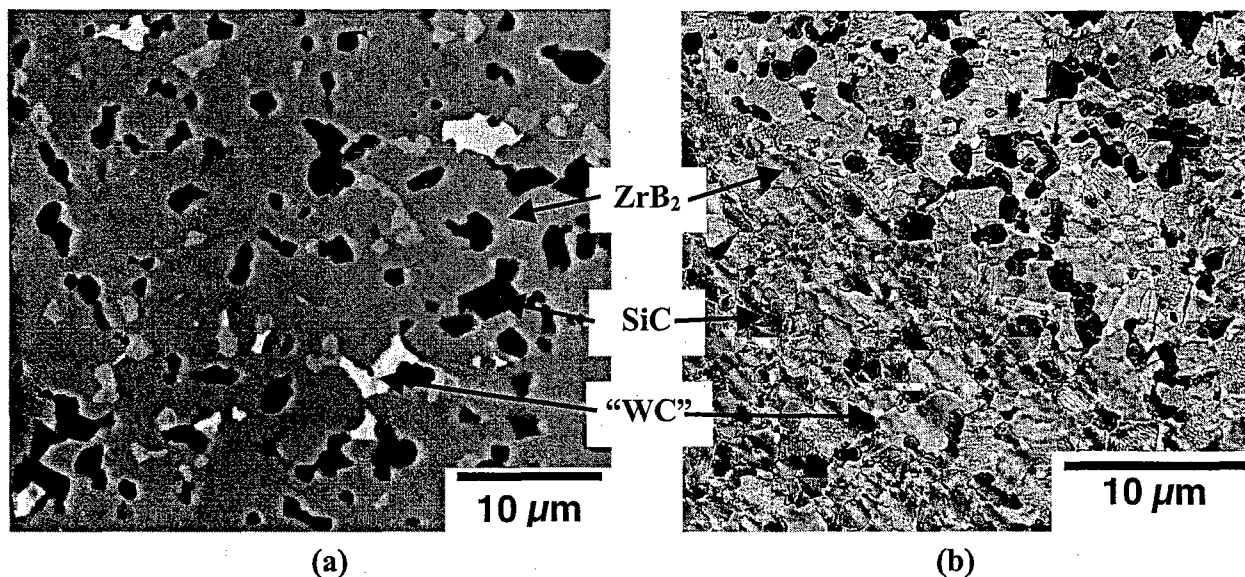


Figure 2. SEM micrographs of (a) polished and (b) polished, thermally etched cross section of ZrB_2 -30% SiC hot pressed at 1900°C.

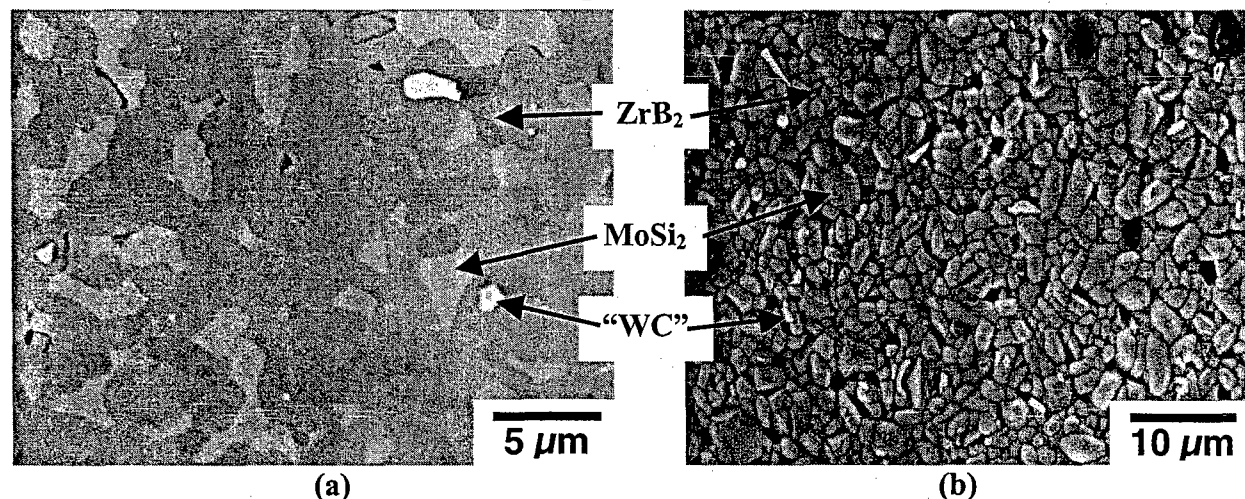


Figure 3. SEM micrographs of (a) polished and (b) polished, thermally etched cross section of ZrB_2 -30% MoSi_2 hot pressed at 1900°C.

Compared to earlier reports, materials produced in this project had significantly higher strengths. In fact, several compositions had strengths in excess of 1 GPa. Based on the strength and oxidation behavior, ZrB_2 containing 30 volume percent SiC was selected to serve as the focus of the remaining processing studies for the program.

The final aspect of the initial processing study was the investigation of the effect of the composition of the milling media on the resulting microstructure and properties of the ZrB_2 -30% SiC material. For this study, four conditions were compared: 1) milling with WC media, which was the baseline composition; 2) milling with SiC media; 3) milling with ZrO_2 media; and 4) milling with SiC media but adding ~2 vol.% WC. Interestingly, the hot pressed density and grain sizes (~3 μm) of the materials did not vary significantly based on the milling media (Table IV and Figure 4). However, the strength varied significantly. Materials prepared using WC, ZrO_2 media, or SiC media with WC additions had strengths over 1 GPa. The strength of the material of the material milled with SiC media was significantly lower, ~800 MPa. Closer examination by SEM revealed the presence of large SiC inclusions in the material (Figure 5).

These SiC inclusions were $\sim 10 \mu\text{m}$ in size and were thought to act as the strength limiting flaws during fracture. Similar SiC agglomerates were not observed in any of the other materials. Subsequent research conducted as part of another program confirmed that size of the SiC particulates did indeed control the strength of the ceramics.

Table IV. Physical and mechanical properties of ZrB_2 -SiC materials prepared from precursor powders that were attrition milled using different milling media.

Milling Media	Relative Density (%)	Hardness (GPa)	Modulus (GPa)	Strength (MPa)
WC	>99	24	506	1089 ± 152
ZrO_2	>99	22	509	1129 ± 87
SiC	95	22	498	817 ± 47
SiC w/WC addn	97	24	500	1106 ± 92

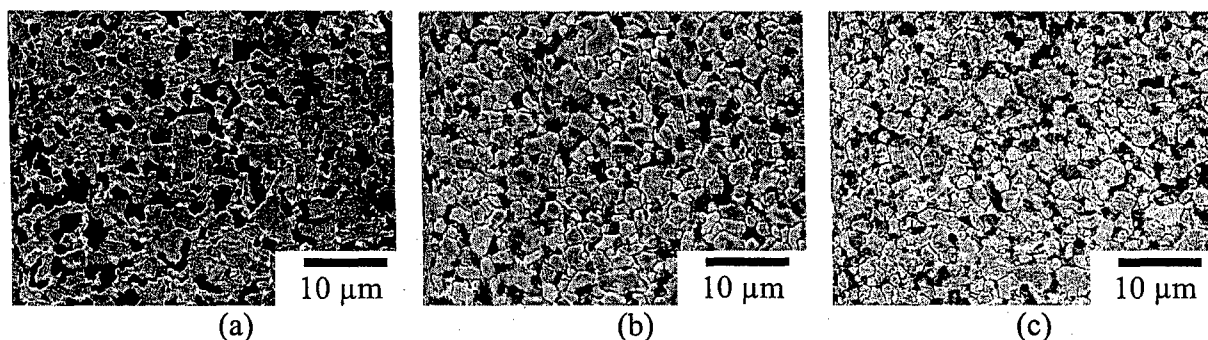


Figure 4. Polished, thermally etched cross sections of ZrB_2 -30 vol.% SiC prepared from powders that were milled with (a) WC, (b), ZrO_2 , and (c) SiC milling media.

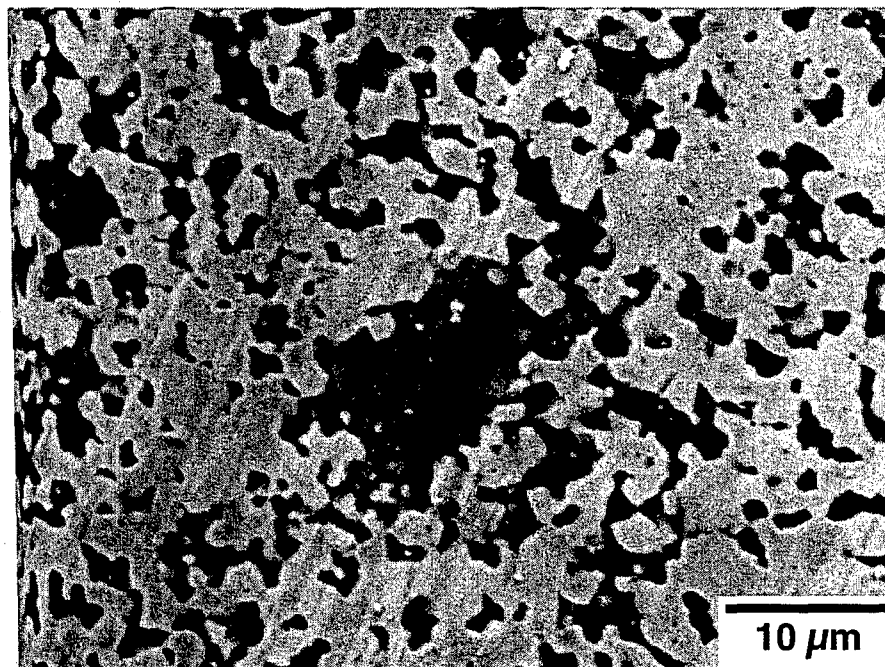


Figure 5. A large SiC agglomerate characteristic of defects in ZrB_2 -30 vol.% SiC prepared from powders that were milled with SiC milling media.

Co-Extrusion Forming

The performance (e.g., fracture behavior or thermal shock behavior) of ceramics can be controlled by manipulating the meso-scale architecture. One method by which this can be accomplished is the fabrication of so-called fibrous monolithic (FM) materials by co-extrusion processing. Typically, FMs consist of a strong, hard cell that constitutes the major proportion of the material and a minor fraction of a weaker cell boundary phase. The co-extrusion process results in the formation of a two dimensional, honeycomb-type architecture as shown in Figure 6. Typical cell sizes range from tens to hundreds of micrometers while the cell boundary thickness can be as small as a few microns. Fibrous monolithic materials have been prepared from a variety of ceramic, intermetallic, and metallic materials. Unlike the incremental gains in performance that are possible when manipulating the intrinsic properties of specific phases, significant performance gains are possible with FMs because their performance is controlled by the relative properties of the cell and cell boundary materials, not the intrinsic properties of the constituent phases. For example, catastrophic failure of WC-based cutting inserts for petroleum drilling bits was eliminated by developing a cellular architecture for the application. In addition, significant improvements in thermal shock performance were achieved for $\text{Si}_3\text{N}_4/\text{BN}$ FMs.

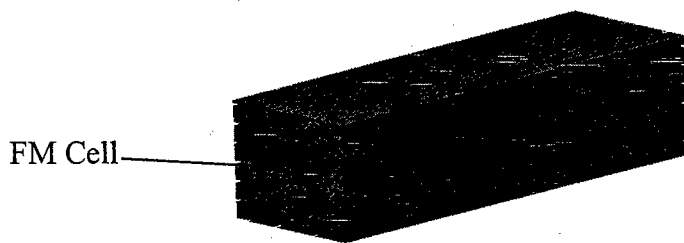


Figure 6. A schematic illustration of the typical fibrous monolithic architecture produced by co-extrusion. The gray material represents the strong, hard cells, while the black represents the cell boundaries.

In this project, ZrB_2 -based FMs were produced. All of the FMs produced as part of this research had ZrB_2 -30 vol.% SiC cells. The cell boundaries were either porous ZrB_2 or a mixture of ZrB_2 and graphite. For the mixtures, graphite content ranged from 0 to 100 volume percent. The cell and cell boundary materials were batched separately. For the cells, ZrB_2 -SiC was prepared by attrition milling the precursor powders for two hours in hexane using WC milling media. The cell boundaries were prepared from a large particle size ($\sim 6 \mu\text{m}$, Grade A, H.C. Starck) ZrB_2 powder and/or carbon (Black Pearls 120, Cabot Corp.). The cell and cell boundary materials were then separately batched with a thermoplastic binder system (polyethylene ethyl acrylate, heavy mineral oil, and methoxypolyethyleneglycol) to produce ceramic powder loaded thermoplastic polymers. The mixtures were then warm ($\sim 150^\circ\text{C}$) pressed into either right regular cylinders (cells) or half moon shaped shells (cell boundaries), which were laminated to form a feedrod for co-extrusion. Feedrods underwent a size reduction of at least a factor of ten during extrusion. After either a single pass or two pass extrusion process, the filaments were assembled into rectangular billets for binder burnout and densification (hot pressing).

The initial UHTC FMs combined ZrB_2 -SiC cells with porous ZrB_2 cell boundaries. The hot pressing process resulted in dense cells surrounded by cell boundaries that contained ~ 28 volume percent porosity (Figure 7). The cells were on the order of $150 \mu\text{m}$ wide and $100 \mu\text{m}$ tall with the cell boundaries $\sim 20 \mu\text{m}$ wide. The strength of the initial FM materials was found to be

~450 MPa. This is less than half of the strength reported for the cell material. These materials showed only catastrophic brittle fracture behavior. Because no crack deflection occurred, the thermal shock performance was similar to monolithic $\text{ZrB}_2\text{-SiC}$ materials. Water quench thermal shock testing conducted according to ASTM C1525 showed a critical ΔT of between 200 and 400°C, compared to a value of ~400°C for monolithic materials.

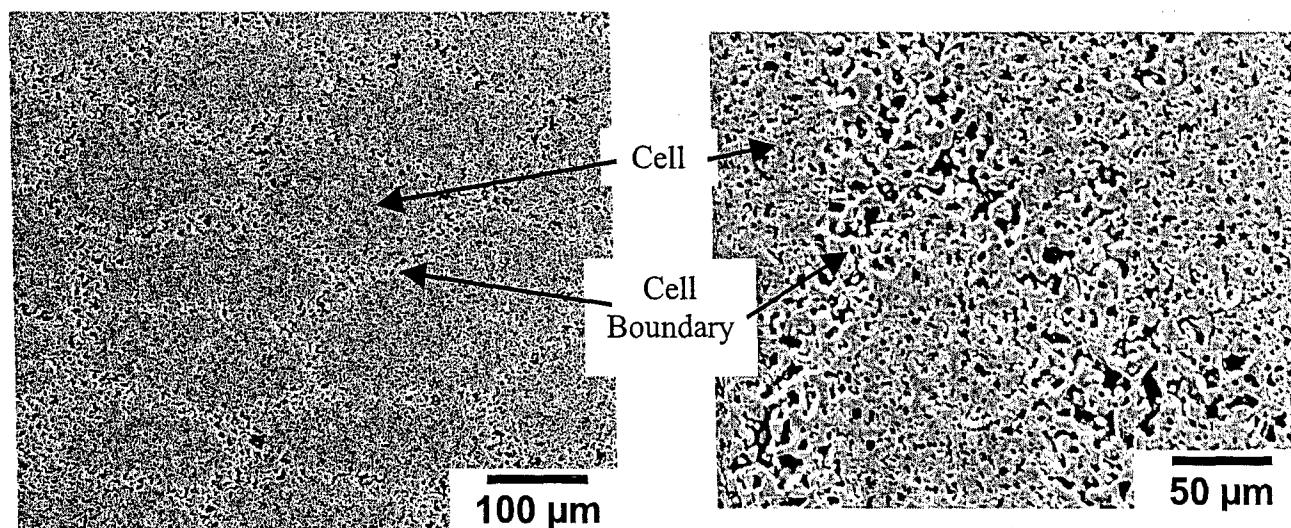


Figure 7. A fibrous monolith architecture consisting of dense $\text{ZrB}_2\text{-SiC}$ cells and porous ZrB_2 cell boundaries prepared by two-pass co-extrusion.

A crack deflection model was developed to understand how the FMs could be modified to promote non-catastrophic failure. The He and Hutchinson criteria for crack deflection in laminates were extended to determine the relative values of strength of the cell boundary and cell needed to promote crack deflection in ZrB_2 -based FMs. In parallel, testing was conducted to evaluate the strength and fracture energy of ZrB_2 -carbon mixtures. The combined analysis resulted in determination of a critical carbon content for the cell boundary phase for crack deflection. The analysis (Figure 8) estimated that a minimum of 85 volume percent carbon was needed in the ZrB_2 -carbon cell boundaries to promote crack deflection. As a result of this analysis, a second generation of structures was fabricated using a single-pass co-extrusion process to produce FMs with $\text{ZrB}_2\text{-SiC}$ cells and ZrB_2 -carbon cell boundaries. These materials had the typical FM cell-cell boundary structure (Figure 9). The strength of the FMs with ZrB_2 -carbon cell boundaries was lower than the strength of first generation of FMs with the strength of the FMs decreasing as the amount of carbon in the cell boundaries increased. For example, a FM with a cell boundary composed of 15 volume percent ZrB_2 and 85 volume percent carbon was 370 MPa compared to ~450 MPa for the porous cell boundary material. However, as the amount of carbon in the cell boundaries increased, the ability of the cell boundaries to deflect cracks increased. This was apparent when observing fracture surfaces. As shown in Figure 10, the fracture surfaces become more highly textured as the amount of carbon in the cell boundaries increases. At 85 vol.% carbon and above, the samples exhibit significant crack deflection that results in non-catastrophic failure behavior in which the specimens demonstrate the ability to retain load after an initial fracture event (Figure 11). Testing is underway to determine if these improved FMs have increased thermal shock performance compared to monolithic $\text{ZrB}_2\text{-SiC}$ and the first generation UHTC FMs that had porous ZrB_2 cell boundaries.

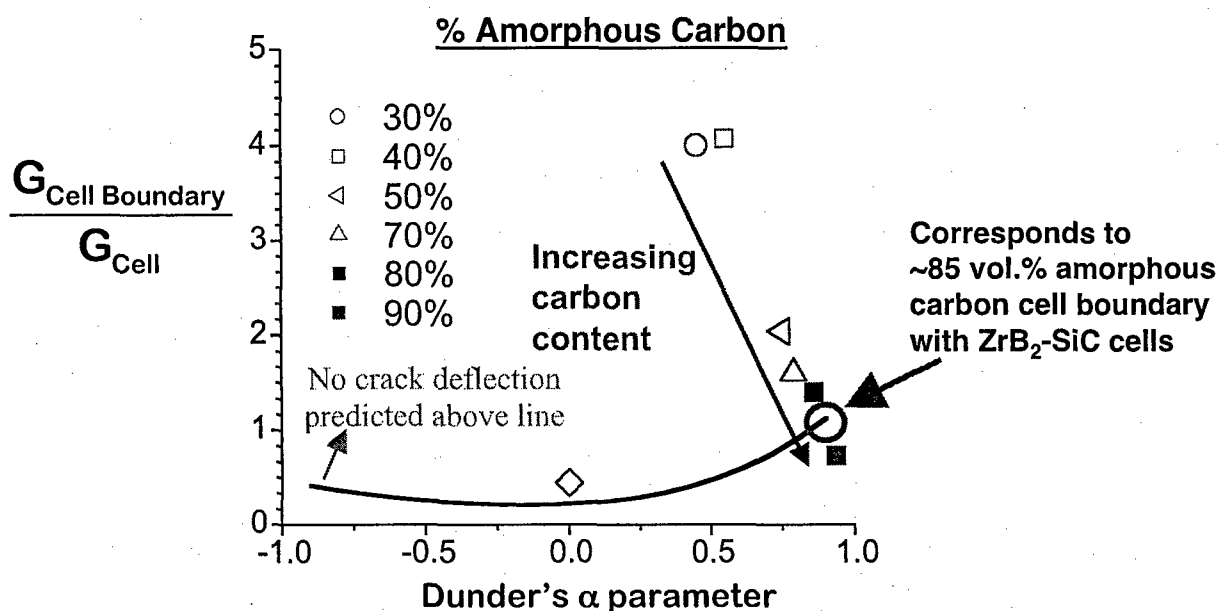


Figure 8. He and Hutchinson analysis of the relative fracture energy of the cell and cell boundary as a function of the relative modulus values of the cells and cell boundaries (Dunder's α) showing that crack deflection should occur when the carbon content of ZrB_2 -carbon cell boundaries is 85 vol.% or greater.

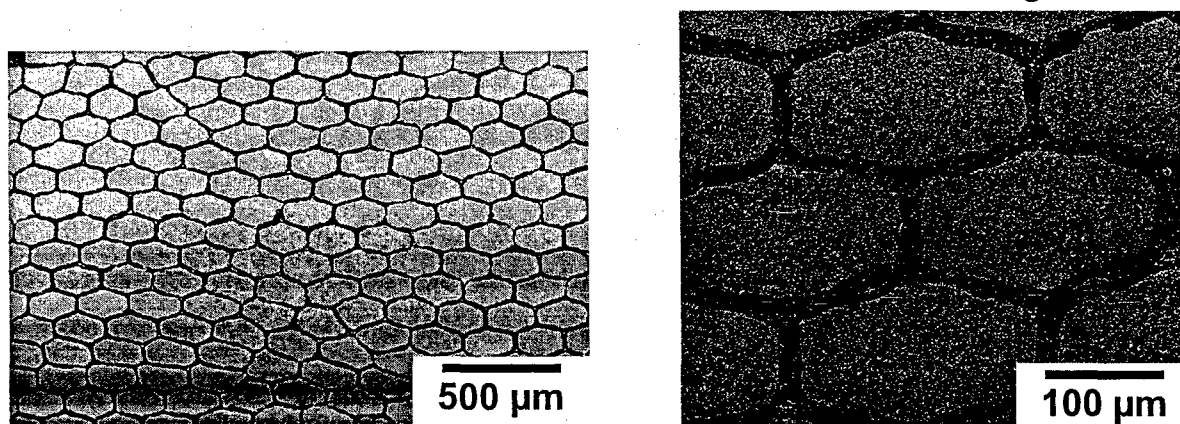


Figure 9. A fibrous monolith architecture consisting of dense ZrB_2 -SiC cells and ZrB_2 -carbon cell boundaries prepared by single-pass co-extrusion.

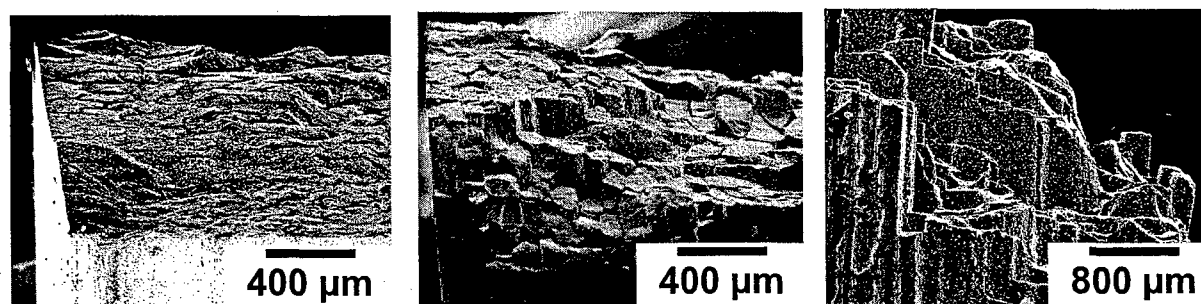


Figure 10. Fracture surfaces of FMs with ZrB_2 -SiC cells and ZrB_2 -carbon cell boundaries containing 30, 40, and 50 vol.% amorphous carbon.

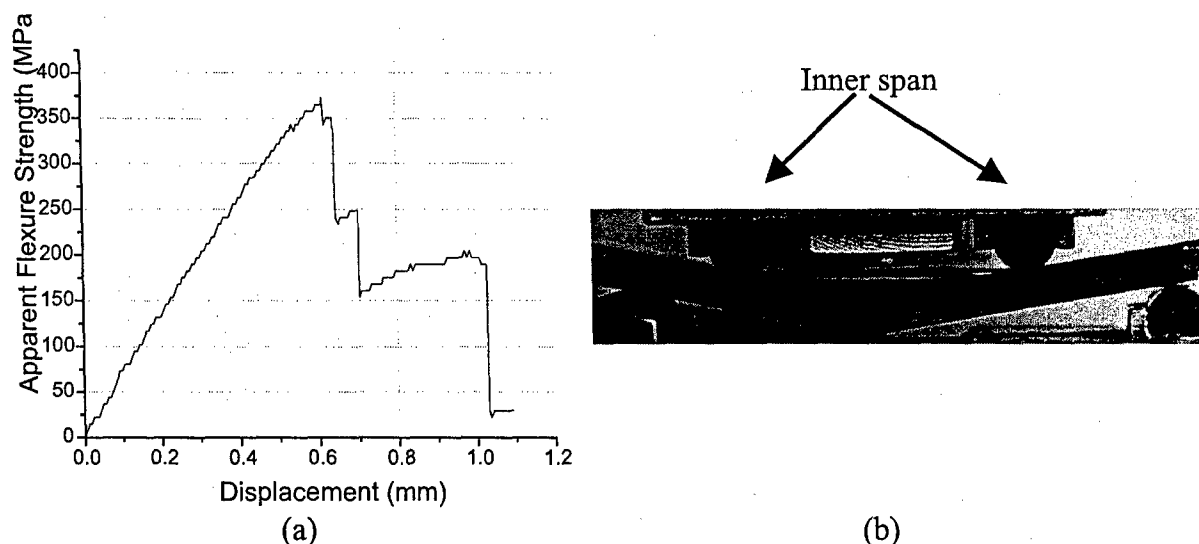


Figure 11. (a) A load-deflection curve and (b) a picture of a fractured specimen of a FM demonstrating non-catastrophic failure.

Pressureless Densification

A process was developed to densify ZrB_2 without the application of external pressure or the deliberate addition of sintering aids. Powders prepared by the method used in the initial processing studies (attrition milled for two hours with WC media) were compacted and sintered using the same temperature-atmosphere profile as the hot pressing procedure described in Table I. Instead of densification under pressure at 1900°C , pellets were sintered for three hours at temperatures ranging from 2000°C to 2150°C . The as-compacted relative density was $\sim 65\%$. As shown in Figure 12a, relative density began to increase at 2100°C . However, the pellets reached only $\sim 72\%$ relative density after sintering at 2150°C for three hours. Sintering time at 2150°C was found to have a strong influence on relative density. Pellets were sintered at 2150°C for times ranging from three to nine hours. Pellets reached $\sim 98\%$ relative density after sintering for nine hours at 2150°C in argon (Figure 12b). Examination of the polished and thermally etched cross sections (Figure 13) showed that the average grain size was $\sim 9 \mu\text{m}$, but a significant number of much larger grains (up to $30 \mu\text{m}$) were observed. The resulting ceramic had an average strength of $\sim 440 \text{ MPa}$, compared to $\sim 560 \text{ MPa}$ for hot pressed ZrB_2 . Development of the sintering process is continuing through a project sponsored by the Air Force Research Laboratory (Grant FA8650-04-C-5704, Dr. Ron Kerans, technical point of contact). The AFOSR-sponsored work was the first report of the sintering of ZrB_2 to high relative density without either the application of external pressure or the addition of liquid phase sintering aids. This research could have a significant impact on the cost of UHTC components since development of pressureless sintering will enable the near-net-shape production of ZrB_2 -based components.

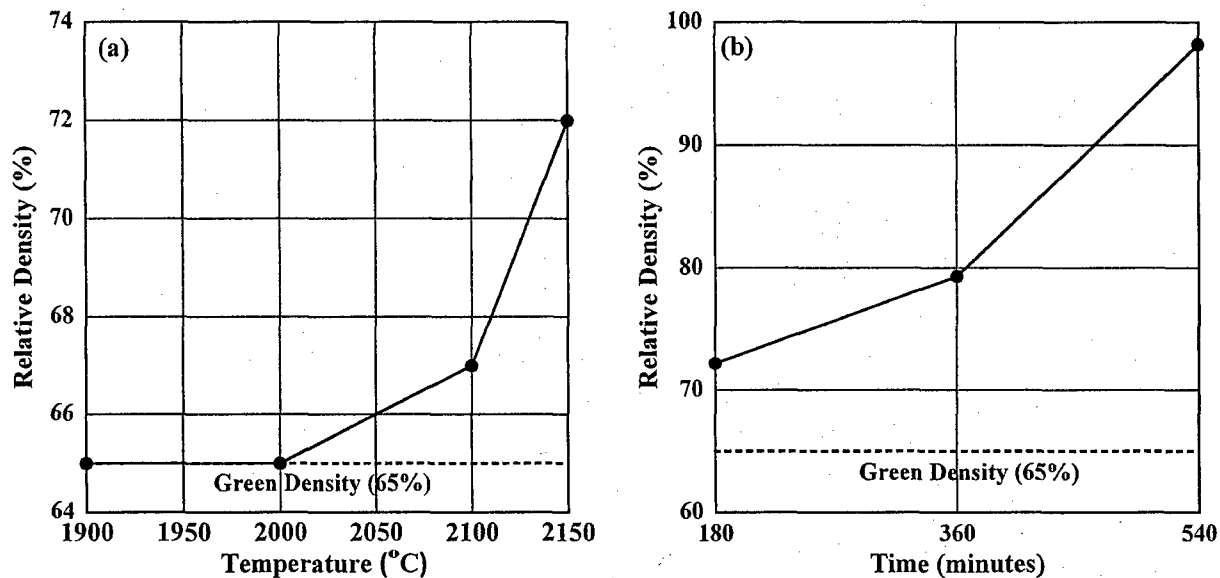


Figure 12. Relative density of ZrB₂ sintered in argon as (a) a function of temperature and (b) a function of hold time at 2150°C.

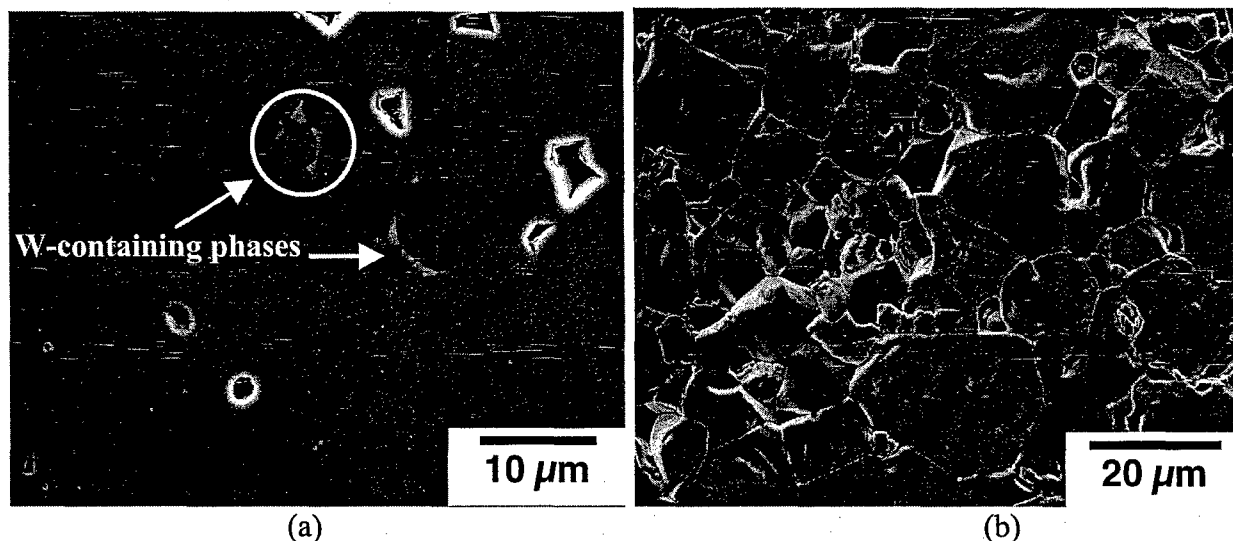


Figure 13. Micrographs of (a) polished and (b) thermally etched cross sections of ZrB₂ densified by pressureless sintering at 2150°C.

Oxidation

A thermodynamic model was developed to understand ZrB₂-SiC oxidation. The model employs a ZrB₂ volatility diagram to explain the formation of a SiC-depleted layer beneath the surface oxide layer that forms when ZrB₂-SiC is exposed to air at 1500°C. To create the model, a ZrB₂-SiC volatility diagram was produced (Figure 14) by overlapping diagrams for ZrB₂ and SiC that were calculated separately. For exposure of ZrB₂-SiC to air (Log pO₂ = -0.67) at 1500°C, the diagram shows that ZrO₂, SiO₂, and B₂O₃ should form. The vapor pressure of B₂O₃ is high (Log p = -2.5 or P = 320 Pa), indicating that B₂O₃ should evaporate at 1500°C. The ZrO₂ is porous and, alone, does not protect the underlying ZrB₂-SiC from further oxidation. Thus, the SiO₂ provides passive oxidation protection to ZrB₂-SiC. The source for the Si that forms the SiO₂ layer is the SiC in the underlying ZrB₂-SiC. Based on the oxygen concentration gradient

that exists across the outer oxide scale, the oxygen activity beneath the scale is expected to be low enough to promote the active oxidation of SiC. During exposure to air at 1500°C, the thickness of both the SiO₂ layer and the SiC-depleted layer continue to increase as a function of time. The overall process exhibits passive oxidation behavior with parabolic ($t^{1/2}$) kinetics due to the growth of the outer SiO₂ scale during exposure. A schematic showing the layered surface structure that develops along with the predicted oxygen partial pressures and the relative motion of the interfaces is shown in Figure 15.

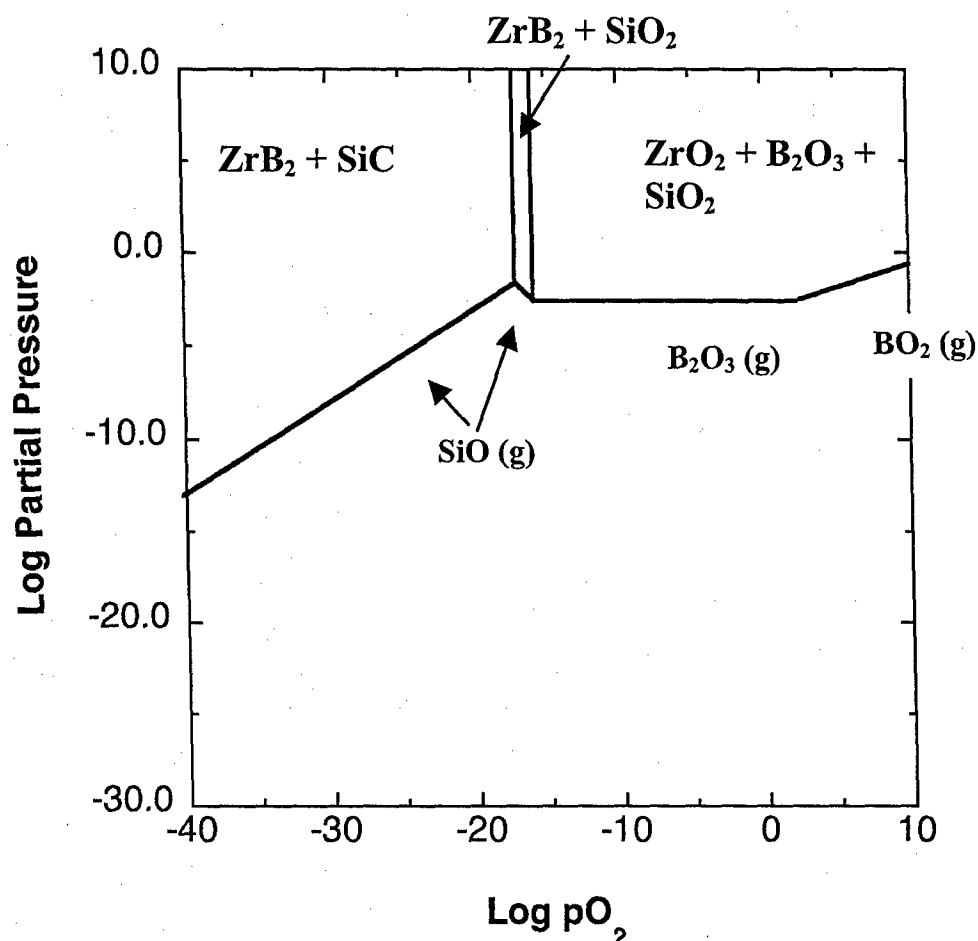


Figure 14. A volatility diagram for the combined ZrB₂ and SiC system showing the vapor pressure of the predominant gaseous species as a function of oxygen partial pressure at 1500°C.

Reactive Processing

Reactive processing methods were developed to prepare ZrB₂ and ZrB₂-SiC. Previous research has shown that some of the advantages of reactive processing are: 1) reduced processing temperature; 2) use of cheaper, more abundant precursors; 3) development of favorable microstructures; and 4) net shape forming capability. For UHTCs, another potential benefit is the improvement of high temperature mechanical behavior due to the minimization of deleterious oxide impurities. The reactive hot pressing effort used Zr and B as precursors to form ZrB₂ and to produce other ZrB₂-based ceramics. Initial experiments focused on understanding and controlling the reaction of Zr and B. Later work focused on reactive hot pressing of ZrB₂-SiC.

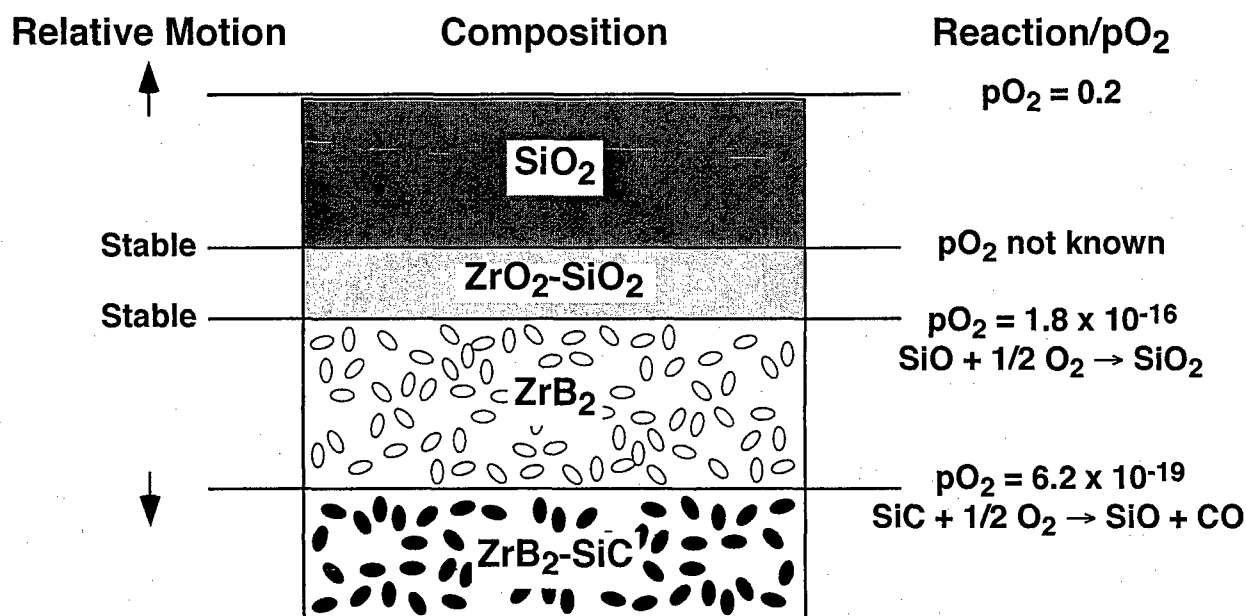
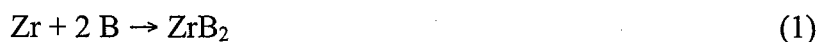


Figure 15. A schematic illustration of the layered structure that develops on the surface of ZrB_2 -SiC during oxidation at 1500°C in air. The diagram shows the oxygen partial pressures and the relative motion of the interfaces.

ZrB_2 was formed from elemental Zr and B. The Zr powder (Alfa Aesar, Ward Hill, MA) had a purity of 98% and a reported particle size of less than 325 mesh. The B powder (Reade Materials, Reno, NV) had a reported purity of 99% and particle size of 50 nm. Batches were prepared using 80.7 weight percent Zr and 19.3 weight percent B to produce ZrB_2 by Reaction 1. After batching, powders were attrition milled for two hours in hexane using WC milling media and a speed of 600 rpm. Powders were dried in vacuum at room temperature to minimize oxidation of the Zr during drying.



Milled powders were hot pressed (HP3060, Thermal Technology, Santa Rosa, CA) in a graphite die lined with graphite foil that was coated with boron nitride. Samples were densified according to the heating schedule given in Table V. An extremely slow heating rate ($2^\circ\text{C}/\text{min}$) and a six hour isothermal hold at 600°C were used to prevent the ignition of a self-propagating reaction during hot pressing. When the die temperature reached the final processing temperature, a uniaxial load of 40 MPa was applied for 45 minutes. Specimens were cooled at $\sim 20^\circ\text{C}/\text{min}$ and the load was removed when the specimen temperature dropped at least 300°C below the final densification temperature.

Silicon carbide was incorporated into reactively processed materials by adding SiC powder to a mixture of Zr and B. These materials were densified using the process outlined in Table V, except that the final hold temperature was varied to assess the effect of hot pressing temperature on densification.

Initial studies of Zr-B reaction couples indicated that Reaction 1 proceeded by the diffusion of B into Zr. Because Reaction 1 is highly exothermic ($\Delta H_{\text{rxn}} = -323 \text{ kJ}$ at 298 K), ignition of a self-propagating combustion reaction occurred in some of the initial experiments. Determination of the reaction onset temperature ($\sim 600^\circ\text{C}$ by differential thermal analysis) combined with reduction of the initial heating rate and inclusion of an isothermal hold near the

reaction onset temperature allowed for processing of these materials without ignition of a self-propagating reaction.

Table V. Heating schedule for reactively hot pressed ZrB_2 ceramics

Temperature ($^{\circ}\text{C}$)	Ramp Rate ($^{\circ}\text{C}/\text{min}$)	Hold time (min)	Atmosphere
RT-600	2	360	Vacuum
600-1000	5	60	Vacuum
1000-1450	10	60	Vacuum
1450-1650	3	60	Vacuum
1650-2100	50	45	Helium

The relative density of reactively hot pressed ZrB_2 ranged from 73 to 98% as the hot pressing temperature increased from 1900°C to 2100°C . Cross sections of the specimens revealed that some regions were dense, but others remained porous. This behavior was attributed to the development of hot spots within the billet due to the extremely exothermic nature of Reaction 1. As the hot pressing temperature increased, the dense regions evolved from isolated, randomly distributed regions (Figure 16a) to a core-shell type geometry (Figure 16b).

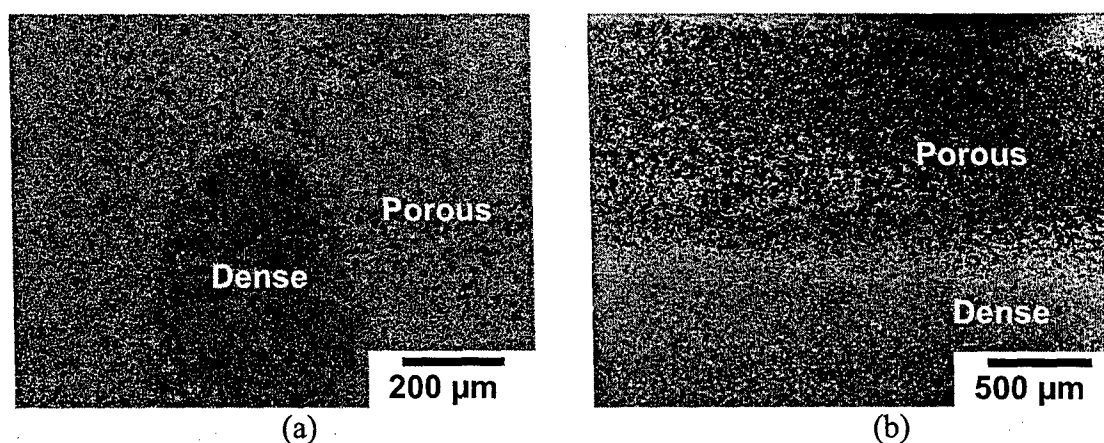


Figure 16. Cross sections of ZrB_2 produced by reactive hot pressing at (a) 1900°C and (b) 2050°C .

The microstructure and mechanical properties of reactively hot pressed ZrB_2 were examined. Figure 11 shows a typical microstructure of a specimen processed at 2100°C . The average grain size was $\sim 14\ \mu\text{m}$ with a maximum grain size of nearly $40\ \mu\text{m}$. This is much larger than the grain sizes found for ZrB_2 hot pressed from commercial precursors ($\sim 6\ \mu\text{m}$). Grain size is thought to increase due to the higher processing temperature compared to conventional ZrB_2 and the lack of any second phases in the grain boundaries that could pin grain growth (e.g., WC or SiC). The mechanical properties of the reactively hot pressed ZrB_2 are summarized in Table VI. The strength of the material was $\sim 250\ \text{MPa}$ compared to $565\ \text{MPa}$ reported for conventional materials. The large grain size of the ZrB_2 produced by reactive hot pressing is thought to be the cause of the reduced strengths relative to the measured strengths of materials produced by conventional hot pressing.

Table VI. Physical and mechanical properties of ZrB₂ prepared by reactive hot pressing compared to conventional hot pressing.

	Hardness (GPa)	Young's Modulus (GPa)	Strength (MPa)
RHP ZrB₂	492	22	250 ± 18
Conventional HP	489	23	565 ± 53

The addition of 30 volume percent SiC to the Zr and B powders used for reaction hot pressing led to a substantial change in the densification behavior and the resulting microstructure and properties. The addition of SiC reduced the temperature required for densification. Near theoretical density was achieved for hot pressing at temperatures as low as 1650°C. Analysis of particle size and strain as a function of temperature using Williamson-Hall plots of x-ray diffraction data showed that reactively formed ZrB₂ in ZrB₂-SiC batches had a mean particle size of ~10 nm and a residual non-uniform strain compressive strain of ~0.21% at the formation temperature (600°C). The combination of the fine particle size and the high residual strain were thought to be the primary driving forces for the enhanced densification. As a consequence of the extremely fine ZrB₂ crystallites formed by the reactive process, the grain size of the final ZrB₂-SiC ceramic was ~1.5 µm, which is about half of the grain size observed for ZrB₂-SiC produced by conventional hot pressing. For ZrB₂-SiC prepared by reactive hot pressing of Zr, B, and SiC at 1750°C, the four point bend strength was ~800 MPa, which is about 250 MPa lower than conventionally prepared material. The reduction in strength in these materials was attributed to surface flaws that developed during machining, which appear to form due to the low fracture toughness of the material. The mechanical properties for ZrB₂-SiC prepared by reactive hot pressing are summarized in Table VII.

Table VII. The physical and mechanical properties of ZrB₂-30% SiC prepared by reactive hot pressing (RHP) compared to conventional hot pressing (HP).

	Processing Temperature (°C)	Grain Size (µm)	Vickers' Hardness (GPa)	Young's Modulus (GPa)	Strength (MPa)	Fracture Toughness (MPa·m ^{1/2})
RHP	1750°C	1.5	27	510	800	3.2
HP	1900°C	3	23	484	1089	5.2

Summary and Impact

The major outcomes and impacts of this research can be summarized as follows:

1. As part of this project, ZrB₂-based ceramics were developed with strengths higher than any previously reported. For ZrB₂-SiC (20 or 30 vol.% SiC) and ZrB₂-MoSi₂ (20 or 30 vol.% MoSi₂), strengths were in excess of 1 GPa. The high strengths were attributed to fine grain size and high purity of the final ceramic. The development of higher strength ceramics will increase the design margin possible with UHTC parts and allow for their use in a wider variety of military systems.
2. The size and distribution of SiC particulates in the ZrB₂ matrix were found to affect strength. When the SiC particle size was small (<5 µm) and the SiC particulates were well distributed in the ZrB₂ matrix, strength was more than 1 GPa. When large (10 µm or

larger) SiC particles or agglomerates were present, strength dropped significantly. This research has shown that distribution of the second phase has a significant impact on the strength of the resulting material. Thus, proper powder processing procedures are vital in the production of high strength UHTCs.

3. Co-extrusion processing was used to produce UHTC fibrous monoliths. Non-catastrophic failure behavior was demonstrated in which a significant fraction of the pre-failure load could be supported after an initial fracture event. Modeling suggested that the strength of the porous ZrB_2 or ZrB_2 -carbon cell boundaries relative to the ZrB_2 -SiC cells controlled the fracture behavior based on the ability of the cell boundaries to deflect cracks. This research could ultimately lead to significant improvement in thermal shock performance of UHTC components since performance can be controlled by meso-structural features, not the inherent thermo-mechanical properties of the ceramic.
4. A pressureless sintering process was developed whereby ZrB_2 could be densified without the application of external pressure or liquid phase sintering additives. This process will enable the production of near-net-shape ZrB_2 parts without the need for expensive and time consuming diamond machining. Pressureless sintering will enable rapid, low-cost manufacturing of UHTC components.
5. The fundamental oxidation behavior of ZrB_2 -SiC was examined by calculating volatility diagrams. A four step reaction sequence was proposed for the formation of a SiC-depleted layer during oxidation of ZrB_2 -SiC in air at 1500°C . This research should enable the development of compositions with improved oxidation resistance and the interpretation of results from static oxidation testing. In addition, the thermodynamic models can easily be extended to interpret experimental results related to the response of ZrB_2 and/or ZrB_2 -SiC to other environments of interest such as monatomic oxygen, combustion chambers, and arc-heater testing.
6. Reaction-based processing methods were developed to produce ZrB_2 and ZrB_2 -SiC. Fundamental reaction behavior was studied using the reaction of Zr and B to form ZrB_2 . This knowledge was applied to produce ZrB_2 -SiC, which is the relevant composition for target applications. The major outcome of this aspect of the project was the production of dense ZrB_2 -SiC at temperatures as low as 1650°C . Thus, this research has provided a combined reaction synthesis/densification process that could lead to significant reductions in the cost of fabricating UHTC components.
7. This project did not fully explore potential synergies among reactive processing, co-extrusion, and pressureless sintering. However, a combination of two or more of these processing methods could lead to significant advances in the state-of-the-art. For example, the combination of reactive processing and pressureless sintering could further reduce the temperatures required for densification while enabling the fabrication of near-net shape components with improved high temperature performance.

PERSONNEL SUPPORTED

Table VIII. Personnel supported during this project.

Name	Title/Role	Level of Support
Dr. Bill Fahrenholtz	Co-PI	1 mo. summer salary/yr
Dr. Greg Hilmas	Co-PI	1 mo. summer salary/yr
Jim Zimmermann	Grad. research assistant, co-extrusion	50% time GRA
Adam Chamberlain	Grad. fellow, reactive processing	No salary*
Michelle Schaeffler	Undergraduate, hot pressing	10 hrs/wk, 2004-2005
Cecilia Fernandez	Undergraduate, co-extrusion	10 hrs/wk, 2004-2005
Stefanie Jaeschke	Undergraduate, hot pressing	40 hrs/wk, summer 2003

* A.C.'s salary is support on a grant from the U.S. Department of Education.

PUBLICATIONS AND PRESENTATIONS

Peer-Reviewed Publications

1. W.G. Fahrenholtz, "Thermodynamic Analysis of ZrB_2 -SiC Oxidation: Formation of a SiC-Depleted Region," submitted to Journal of the American Ceramic Society, February 2006.
2. W.G. Fahrenholtz, "Reactive Processing in Ceramic-Based Systems," International Journal of Applied Ceramic Technology, 3(1) 1-12 (2006).
3. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Pressureless Sintering of Zirconium Diboride," Journal of the American Ceramic Society, 89(2) 450-456 (2006).
4. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Oxidation of ZrB_2 -SiC Ceramics Under Atmospheric and Reentry Conditions," Refractories Applications Transactions, 1(2) 1-8 (2005).
5. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "High Strength ZrB_2 -Based Ceramics," Journal of the American Ceramic Society, 87(6) 1170-1172 (2004).
6. W.G. Fahrenholtz, G.E. Hilmas, A.L. Chamberlain, and J.W. Zimmermann, "Processing and Characterization of ZrB_2 -Based Monolithic and Fibrous Monolithic Ceramics," Journal of Materials Science, 39(19) 5951-5957 (2004). (UMR photo on cover of issue)
7. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Characterization of Zirconium Diboride Ceramics for Thermal Protections Systems," Key Engineering Materials, 264-268, 493-496 (2004).
8. A. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Characterization of Zirconium Diboride-Molybdenum Disilicide Ceramics," pp. 299-308 in Advances in Ceramic Matrix Composites IX, Ceramic Transactions, Volume 153, ed. by N.P. Bansal, J.P. Singh, W.M. Kriven, and H. Schneider, The American Ceramic Society, Westerville, OH (2003).

Thesis/Dissertation

Papers 3 and 5 from the list above along with two additional manuscripts will be combined to constitute the PhD dissertation of Adam Chamberlain. An executive summary of the planned dissertation is included as Appendix B.

The PhD research of Jim Zimmermann was also supported on this project. Jim's efforts have focused on the development of ZrB_2 -based fibrous monolithic ceramics with improved thermal shock performance. The manuscripts that will constitute his dissertation have not yet been drafted, but will acknowledge the financial support of this program when completed. An executive summary of the planned dissertation is included as Appendix C.

Invited Presentations

1. W.G. Fahrenholtz and G.E. Hilmas, "Structure-Property Relations in Monolithic and Fibrous Monolithic ZrB_2 -Based Ceramics," UNITECR '05, November 8-11, 2005, Orlando, FL.
2. W.G. Fahrenholtz, "Ultra-High Temperature Ceramics," Global Research Learning Community of the UMR Residential College, Univ. of Missouri-Rolla, April 26, 2005.
3. W.G. Fahrenholtz, "Reactive Processing in Ceramic-Based Systems," 107th Annual Meeting of the American Ceramic Society, April 10-13, 2005, Baltimore, MD.
4. W.G. Fahrenholtz, "Ultra-High Temperature Ceramics for Hypersonic Applications," Department of Chemical Engineering Seminar, Oklahoma State University, March 24, 2005.
5. G.E. Hilmas, "Ultra-High Temperature Ceramics and Ceramic Composites," AFRL - Materials Directorate, November 8, 2004, Dayton, OH.
6. G.E. Hilmas and W.G. Fahrenholtz, "Ultra-High Temperature Ceramics and Ceramic Composites," High Temperature Materials Group, Boeing-St. Louis, July 15, 2004.

Contributed Presentations

1. J.W. Zimmermann, G.E. Hilmas, and W.G. Fahrenholtz, "Water Quench Thermal Shock Testing of ZrB_2 -SiC," 30th Annual International Conference of Advanced Ceramics and Composites, January 22-26, 2006, Cocoa Beach, FL.
2. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Reactive Processing of Zirconium Diboride Ceramics," 30th Annual International Conference of Advanced Ceramics and Composites, January 22-26, 2006, Cocoa Beach, FL.
3. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Reactive Processing of Zirconium Diboride Ceramics," 6th PAC-RIM Conference on Ceramic and Glass Technology, September 12-16, 2005, Kapalua, Maui, Hawaii.
4. J.W. Zimmermann, G.E. Hilmas, and W.G. Fahrenholtz, "Zirconium Diboride Based Fibrous Monolithic Ceramics," 6th PAC-RIM Conference on Ceramic and Glass Technology, September 12-16, 2005, Kapalua, Maui, Hawaii.
5. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Pressureless Sintering of ZrB_2 ," 29th Annual International Conference of Advanced Ceramics and Composites, January 23-27, 2005, Cocoa Beach, FL.
6. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Reactive Hot Pressing of ZrB_2 ," 29th Annual International Conference of Advanced Ceramics and Composites, January 23-27, 2005, Cocoa Beach, FL.
7. J.W. Zimmerman, G.E. Hilmas, and W.G. Fahrenholtz, "UHTC Fibrous Monolithic Ceramics with a Carbon-Modified Interphase," 29th Annual International Conference of Advanced Ceramics and Composites, January 23-27, 2005, Cocoa Beach, FL.
8. J.W. Zimmermann, G.E. Hilmas, and W.G. Fahrenholtz, "Non-Catastrophic UHTC Fibrous Monolith Composites," Pacific Coast Regional Meeting of the American Ceramic Society, Seattle, WA, September 12-16, 2004.
9. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Phase Equilibria in the Zirconium-Boron System," Pacific Coast Regional Meeting of the American Ceramic Society, Seattle, WA, September 12-16, 2004.

10. J.W. Zimmermann, W.G. Fahrenholtz, and G.E. Hilmas, "Processing and Properties of ZrB₂-SiC/Porous ZrB₂ Fibrous Monoliths," 28th Annual International Conference of Advanced Ceramics and Composites, January 25-29, 2004, Cocoa Beach, FL.
11. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Processing Effects on ZrB₂-SiC Ceramics," 28th Annual International Conference of Advanced Ceramics and Composites, January 25-29, 2004, Cocoa Beach, FL.
12. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Oxidation of Zirconium Diboride-Silicon Carbide Ceramics Under Atmospheric and Reentry Conditions," presented at the 28th Meeting on Composites, Materials, and Structures, January 25-29, 2004, Cocoa Beach, FL.
13. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Characterization of Zirconium Diboride Based Composites," Pacific Coast Regional Meeting of the American Ceramic Society, October 19-22, 2003, Oakland, CA.
14. J.W. Zimmermann, G.E. Hilmas, and W.G. Fahrenholtz, "Zirconium Diboride Fibrous Monolith Composites," Pacific Coast Regional Meeting of the American Ceramic Society, October 19-22, 2003, Oakland, CA.
15. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Characterization of Zirconium Diboride Ceramics for Thermal Protections Systems," presented at the 8th meeting of the European Ceramic Society, June 29-July 3, 2003, Istanbul, Turkey.
16. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Characterization of Zirconium Diboride with Molybdenum Disilicide Additives," presented at the 105th Annual Meeting of the American Ceramic Society, April 27-April 30, 2003, Nashville, TN.
17. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Characterization of Zirconium Diboride with Molybdenum Disilicide Additives," presented at the 27th Meeting on Composites, Materials, and Structures, January 27-30, 2003, Cocoa Beach, Florida

Posters

1. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and J.W. Zimmermann, "Performance of Zirconium Diboride-Silicon Carbide Composites," Gordon Research Conference on High Temperature Materials, Processes, and Diagnostics, Waterville, ME, August 1-6, 2004.
2. A.L. Chamberlain, J.W. Zimmermann, W.G. Fahrenholtz, and G.E. Hilmas, "Particulate and Functionally Engineered Zirconium Diboride Based Composites for Enhanced Mechanical Behavior," presented at the National Space and Missile Materials Symposium, Seattle, WA, June 21-25, 2004.
3. A.L. Chamberlain, J.W. Zimmermann, W.G. Fahrenholtz, and G.E. Hilmas, "Ultra-High Temperature Ceramics," presented at the UMR Technology Showcase, May 24, 2004.
4. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Characterization of Zirconium Diboride with Silicon Carbide Additives," presented at the 105th Annual Meeting of the American Ceramic Society, April 27-April 30, 2003, Nashville, TN.

Newspapers

1. "Stronger Tiles is Research Goal" in *Kansas City Star*, February 4, 2003.
2. "UMR Work Could Solve Heat Problem," *Springfield (MO) News Leader*, February 5, 2003.
3. "Columbia Explosion Brings Questions" *Northwest Missourian*, February 5, 2003
4. "Research by UMR Ceramic Engineers May Have Value for Future Space Vehicles," *Rolla (MO) Daily News*, February 6, 2003.
5. "UMR Tile Research Receiving Recognition" appeared on the front page of Springfield (MO) Hillcrest High School newspaper *The Herald*, May 23, 2003.

Radio

1. KTTR, Rolla, MO, February 4, 2003.
2. University of Missouri System Radio Interview, February 3, 2003.

Television

1. KTVI Channel 2, St. Louis, MO, February 3, 2003.
2. KMOV Channel 4, St. Louis, MO, February 3, 2003.
3. KSDK Channel 5, St. Louis, MO, February 3, 2003.
4. WDAF Channel 4, Kansas City, MO, February 3, 2003.
5. KYTV Channel 3, Springfield, MO, February 3, 2003.
6. KOMU Channel 8, Columbia, MO, February 3, 2003.
7. KOLR Channel 10, Columbia, MO, February 3, 2003.

Professional/Technical Publications

1. "Stronger Tile, Safer Shuttle," Global News section in American Ceramic Society Bulletin, 82(5) 7 (2003)
2. "Hot Stuff," BMOC Feature in *Design News*, April 2003.
3. "UMR Professors Developing Better Tiles for Future Space Vehicles," MSM-UMR Alumnus, page 16, Spring 2003.
4. "NASA Plans Tile Improvement" *The Engineer*, page 10, February 7, 2003

INTERACTIONS/TRANSITIONS

1. As part of this research, it was discovered that ZrB_2 could be densified by pressureless sintering. Further development of the sintering process was funded in a follow-on project by the Air Force Research Laboratory (Grant FA8650-04-C-5704, Dr. Ron Kerans, technical point of contact). Currently, UMR is fabricating two components using the pressureless sintering process for testing in applications related to Air Force needs. A propulsion component is being fabricated for testing in a scramjet testbed at AFRL and a leading edge section is being fabricated for testing in the large core arc tunnel at Boeing-St. Louis.
2. Samples of UMR's high strength ZrB_2 -SiC were evaluated in the large core arc tunnel at Boeing-St. Louis in November 2005.
3. Samples of UMR's high strength ZrB_2 -SiC were fabricated for high temperature property testing at the Southern Research Institute. Materials were prepared in December 2005 and testing will be conducted during 2006.
4. As part of this program, four manuscripts and six presentations were co-authored with Dr. Donald T. Ellerby, a research scientist at the NASA-Ames Research Center.
5. During the course of this project, three UMR undergraduates held summer appointments at the NASA-Ames Research Center (Kelley O'Hara in 2005, Michelle Schaeffler in 2003 and Adam Chamberlain in 2002).
6. Graduate student Jim Zimmermann spent three months at the Institute of Science and Technology for Ceramics in Faenza, Italy. Jim worked with Drs. Alida Bellosi and Frederic Monteverde, the leading European research group investigating UHTCs. Jim conducted

research on the processing and characterization of UHTCs, including reactive hot pressing and the thermal shock performance of zirconium diboride based ceramics.

7. Interactions are continuing with Dr. Jochen Marschall from SRI International. The UMR team is fabricating ZrB_2 -SiC specimens for impact testing in Dr. Marschall's laboratory. UMR will complete characterization and strength testing of impacted materials. Dr. Marschall also performed laboratory-scale arc-jet testing and impact studies on conventional ZrB_2 -SiC and fibrous monolithic ZrB_2 specimens prepared by UMR.
8. In January 2004, Drs. Hilmas and Fahrenholtz organized a workshop focused on research needs related to ultra-high temperature materials. The "NSF-AFOSR Joint Workshop on Future Ultra-High Temperature Materials" was held January 13 and 14, 2004 at NSF Headquarters in Arlington, VA. The workshop resulted in the production of a report that was disseminated to researchers in the field in hard copy at conferences such as the National Space and Missile Materials Symposium and through a web site (web.umn.edu/~uhtm). A follow-on to the workshop is planned for 2007.
9. The investigative team had significant interactions with the NASA-Ames Research Center. Materials from UMR were tested in the arc jet facility at NASA-Ames on two different occasions.

NEW DISCOVERIES, INVENTIONS, AND PATENT DISCLOSURES

The significant new discoveries from this work are described in the publications listed above and attached to this report.

HONORS/AWARDS

Awards for Dr. Fahrenholtz

1. NSF CAREER award recipient, 2004
2. UMR Faculty Excellence Awards for research, teaching, and service, 2003, 2004
3. UMR Outstanding Teaching Award, 2003
3. MSM/UMR Alumni Association Class of 1942 Teaching Excellence Award, 2003
4. Promotion to Associate Professor with Tenure, 2005
5. MSM/UMR Alumni Association Outstanding Student Advisor Award, 2005
6. UMR School of Materials, Energy, and Earth Resources Award for Excellence in Laboratory Instruction 2004
7. UMR School of Materials, Energy, and Earth Resources Award for Sustained Teaching Excellence, 2003, 2005
8. Outstanding Ceramic Engineering Faculty Member, Ceramic Engineering, 2004-2005
9. Elected to Sigma Xi, The Scientific Research Society, 2004.

Awards for Dr. Hilmas

1. UMR Faculty Excellence Awards for research, teaching, and service, 2003, 2004, 2005
2. UMR Outstanding Teaching Awards, 2003, 2004, 2005
3. UMR School of Materials Energy and Earth Resources Award for Sustained Teaching Excellence, 2003, 2005
4. Promotion to Associate Professor with Tenure, 2004

Awards for Adam Chamberlain

1. Graduate Assistance in Areas of National Need (GAANN) Fellow at UMR, 2002-2005.
2. Department of Ceramic Engineering "Graduate Student of the Year" 2004
3. AFOSR Fellowship to attend the 8th European Ceramic Society in Istanbul (June 2004).

Awards for Michelle Schaeffler

1. First place, undergraduate division, Ceramographic Competition at the Annual Meeting of the American Ceramic Society, 2004
2. Ceramic Engineering "Undergraduate Student of the Year," 2003-2004

APPENDIX A. SUMMARY OF INTERACTIONS WITH ISTE C

This section of the report summarizes interactions between UMR and The Institute for Science and Technology of Ceramics (ISTEC) in Faenza, Italy. The nature of the previous and on-going interactions is reviewed. The major aspects of the technical interactions were the use of reactive processes for the fabrication of $\text{ZrB}_2\text{-SiC}$ and the thermal shock testing of monolithic $\text{ZrB}_2\text{-SiC}$. The thermal shock results were discussed in the body of the report. The results of the reactive processing studies are summarized below.

ISTEC-UMR Interactions

In 2005, Jim Zimmermann, a PhD student at UMR supported by this AFOSR project, spent three months (October-December 2005) in the Institute for Science and Technology of Ceramics (ISTEC). Dr. Alida Bellosi of ISTEC initiated the exchange with an open invitation for anyone from the UMR UHTC group to work at ISTEC. Planning for a visit began at the Cocoa Beach meeting in January 2005, continued by email during the next few months, and was completed at the Annual Meeting of the American Ceramic Society in Baltimore, MD in April 2005. It was decided that UMR student Jim Zimmermann would spend six months at ISTEC. Due to visa issues that arose due to the fact that Jim was not paid to work in Italy, we were forced to reduce the length of his time in Italy to 90 days.

In the time leading up to Jim's experience at ISTEC, the UMR group had frequent email contact with Dr. Bellosi and Dr. Frederic Monteverde to plan the research portion of the interaction. During his visit, Jim submitted reports to UMR that summarized his technical progress. Since returning to UMR, Jim, Dr. Hilmas, and Dr. Fahrenholtz have had frequent communications with the ISTEC personnel regarding results from Jim's time at ISTEC and concerning possible future collaborations. In addition, several joint presentations and manuscripts will result from the interaction. Both institutions are open to future personnel exchanges and continued interaction.

Planned Joint Presentations

1. MS&T '06: " ZrB_2 -25 vol.% SiC Fabricated by Reactive Hot Pressing of ZrH_2 , B_4C , and Si"
2. MS&T'06: "Comparison of ZrB_2 -25% SiC Ceramics Fabricated Using Different Methods"

Planned Collaborative UMR-ISTEC Manuscripts

1. " $\text{ZrB}_2\text{-SiC}$ Ceramics Fabricated *In-Situ*"
2. "Influence of Fabrication Methods on the Mechanical Properties of ZrB_2 -25% SiC Ceramics"

Reactive Processing

Zirconium hydride, silicon, and boron carbide (Table A1) were reacted to form ZrB_2 and SiC. According to the stoichiometry of Reaction A1, the final material should consist of 75 volume percent ZrB_2 and 25 volume percent SiC. Initial reaction experiments found that impurity phases were formed in addition to the desired products. Subsequently, the stoichiometry of the reactants was modified to minimize the formation of the undesired phases. The stoichiometric composition (S), an intermediate composition (I), and a final composition (F) were prepared, as summarized in Table A2.



Table A1. Summary of reactant powder characteristics.

Powder	Particle Size (μm)	Grade	Supplier
ZrH ₂	2	C	Chemetall, Frankfurt, Germany
Si	3.5	HS	H.C. Starck, Newton, MA
B ₄ C	0.8	AX5	H.C. Starck, Newton, MA

Table A2. Stoichiometric, intermediate, and final batch compositions for reactive hot pressing of ZrB₂-SiC.

	Stoichiometric (S)			Intermediate (I)			Final (F)		
	Wt. %	Vol. %	Mol. %	Wt. %	Vol. %	Mol. %	Wt. %	Vol. %	Mol. %
ZrH ₂	69.1	49.5	50	57.1	37.0	39.2	66.7	46.7	47.0
Si	10.4	17.9	25	10.0	15.6	27.8	11.7	19.7	27.3
B ₄ C	20.5	32.6	25	32.9	47.4	38.1	21.6	33.6	25.7

After batching, the powders were ball milled with SiC media in ethanol for 48 hours. The powders were dried by rotary evaporation to minimize segregation. The dried powders were sieved through a 75 mesh screen.

All three compositions were prepared for reaction studies. Initial studies used cylindrical pellets that were 10 mm in diameter and 3 mm high were formed by isostatic pressing at 300 MPa. For the screening studies, pellets were heated at 10°C/min in argon to temperatures ranging from 1150°C to 1450°C (summarized in Table A3) to characterize the reactions. Subsequently, larger specimens that were 60 mm in diameter and 12 mm in height were fabricated for evaluation of microstructure and properties. Based on results with the stoichiometric batch, 1400°C was selected as the temperature for reactions in subsequent reaction studies and in the reactive hot pressing studies.

Table A3. Hold temperatures and times for reactive sintering.

Batch	Run #	Hold Temperature (°C)	Hold Time (hours)
S	1	1150	2
S	2	1300	2
S	3	1400	2
S	4	1450	2
I	1	1400	2
F	1	1400	2

Reactive hot pressing was used to densify S and F materials. Green billets were prepared by cold isostatic pressing at 300 MPa. The green billets were then loaded into BN-coated graphite dies for hot pressing. Specimens were heated inductively in vacuum (~ 1 mTorr) at $\sim 10^\circ\text{C}/\text{min}$. During heating, samples were held at 1400°C for two hours to ensure complete reaction. After the hold, a load of 30 MPa was applied and the specimens were ramped to 1890°C . After a 10 min hold, the pressure was released and the specimens were cooled to room temperature at the natural furnace cooling rate ($\sim 20^\circ\text{C}/\text{min}$).

The reaction products were determined using x-ray diffraction analysis. Reacted pellets were crushed in an agate mortar with a zirconia pestle. Diffraction patterns were collected from 3 to 90 degrees two theta using a step size of 0.03 degrees and a count time of 1 second at each step. Microstructures were examined using scanning electron microscopy (SEM) of polished cross sections. Image analysis was employed to determine the relative percentages of each phase in the microstructure. Phases were also analyzed using energy dispersive spectroscopy (EDS) to determine chemical compositions.

X-ray diffraction analysis indicated that ZrB_2 formed in all of the stoichiometric batches at all processing temperatures. At lower temperatures, ZrC formed in preference to SiC . As the processing temperature increased, the relative amount of SiC increased (Figure A1). In addition to the desired phases (ZrB_2 and SiC), all S specimens contained ZrC and ZrO_2 . The presence of ZrO_2 and ZrC and the absence of B-containing impurity phases implies that boron was lost during processing. This is probably due to evaporation of B_2O_3 , which is an oxide impurity on the B_4C powder. Another indication that B_2O_3 is lost during processing is the greater-than-expected mass loss during heating. About 1.5 weight percent mass loss was expected based on the decomposition of ZrH_2 during processing. However, mass losses as high as ~ 2.8 weight percent were measured for materials reacted at 1450°C .

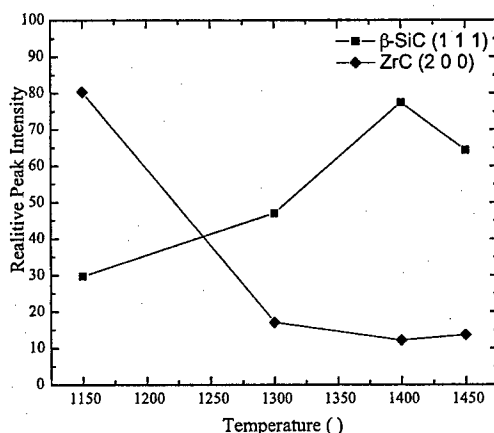


Figure A1. Relative amounts of ZrC and SiC formed as a function of temperature in reaction processed specimens prepared from the stoichiometric composition.

The stoichiometric powder was densified by reactive hot pressing. As shown in Figure A2, the SiC is well dispersed in the ZrB_2 matrix. The density of the reactively hot pressed material was $\sim 5.27 \text{ g}/\text{cm}^3$, which is $\sim 98\%$ relative density based on the expected amounts of ZrB_2 and SiC . Areal analysis indicated that the SiC content of the material was $\sim 20\%$, lower than the 25% expected based on the stoichiometry of Reaction A1. Some of the discrepancy in Si content could be due to partial oxidation of the Si precursor, which would reduce the amount of Si added per unit mass. In addition, some Si may be lost during processing as SiO (g) .

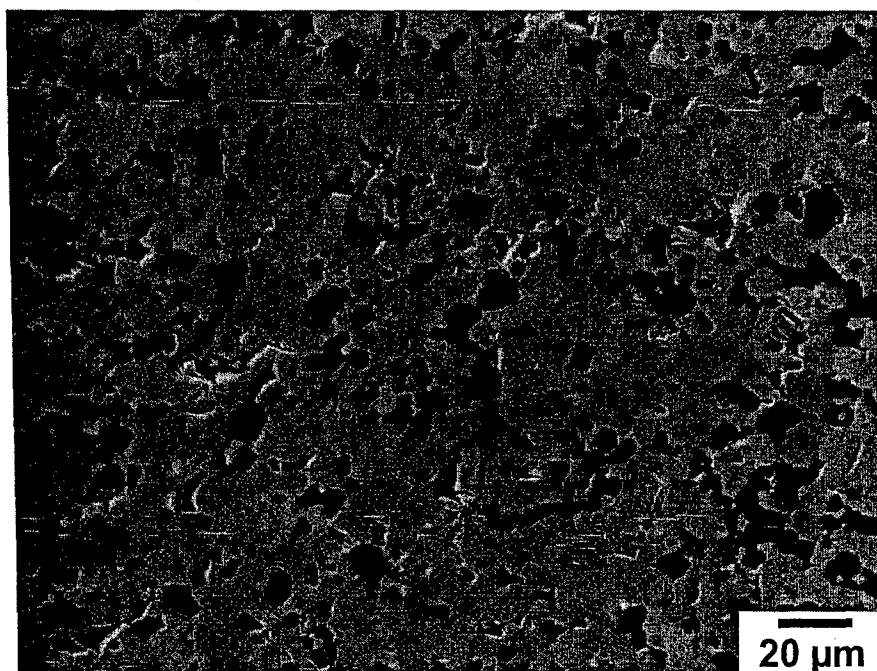


Figure A2. Microstructure of $\text{ZrB}_2\text{-SiC}$ produced by reactive hot pressing of the stoichiometric precursor powder.

To reduce the amount of ZrO_2 and ZrC in the final parts, a second precursor composition was formulated. Both the Si to Zr ratio and the B_4C to Zr ratio were increased in the intermediate batch (composition (I) in Table A2). When composition I was heated to 1400°C for two hours, XRD analysis found no evidence of ZrC or ZrO_2 formation (Figure A3). Analysis of the peak heights for unreacted and reacted powders indicated that $\sim 60\%$ of the B_4C in composition I was consumed by reaction upon heating to 1400°C . Based on this analysis, a final batch formulation (F) was prepared with a lower B_4C content.

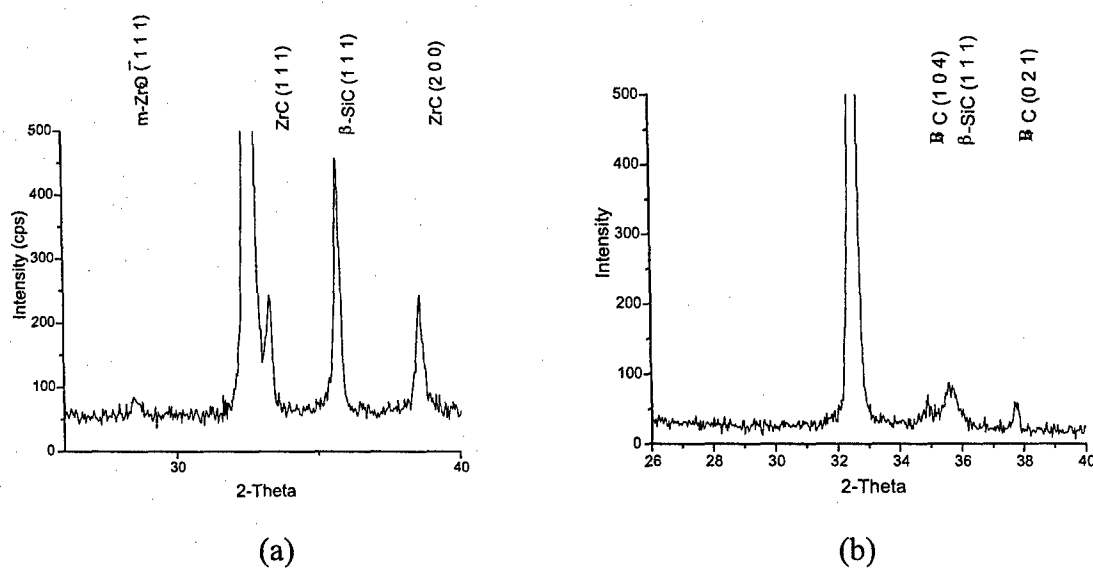


Figure A3. XRD patterns for (a) the stoichiometric and (b) the intermediate batches indicating that excess Si and B_4C reduced ZrO_2 and ZrC formation.

X-ray diffraction analysis of Batch F powders heated to 1400°C (not shown) indicated that ZrB_2 and SiC were the only crystalline phases present. Batch F was then densified by reactive hot pressing. The final density of the material reached 5.37 g/cm³, ~100% relative density, after hot pressing at 1890°C for 10 minutes. The SiC was well-distributed in the ZrB_2 matrix (Figure A4). Areal analysis of SEM images confirmed that the SiC content was ~25 volume percent. In addition, the amount of retained B_4C was estimated to be less than 1 volume percent. Further collaboration between ISTECH and UMR is planned to complete more detailed mechanical property analysis (including high temperature strength testing) and characterization of reaction hot pressed ZrB_2 - SiC . A manuscript is planned to compare the microstructure and properties of ZrB_2 -25% SiC prepared by reactive hot pressing to materials prepared by conventional processes.

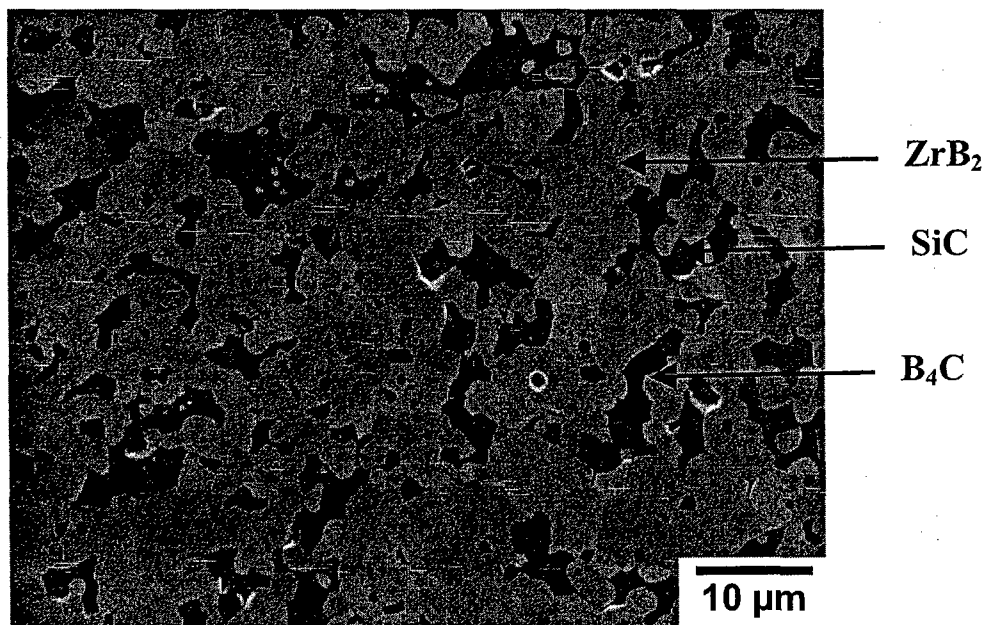


Figure A4. SEM image of a polished cross section of ZrB_2 - SiC that was produced by reactive hot pressing showing ~1 vol.% B_4C along with ZrB_2 and SiC .

APPENDIX B. DISSERTATION OF ADAM CHAMBERLAIN

Adam Chamberlain has selected to complete his dissertation using the "publication" option available at UMR. Essentially, his dissertation will consist of four submitted or published papers with an introduction, review of the relevant literature, an overall summary, and suggestions for future work. As discussed below, two papers that have already been published will be combined with two additional manuscripts to form the body of Adam's dissertation. After approval of his dissertation committee, a copy of the entire dissertation will be available through the Curtis Laws Wilson Library at the University of Missouri-Rolla.

Adam Chamberlain's Ph.D. research has focused on the fabrication and improved performance of zirconium diboride (ZrB_2) ceramics. Improvements in the performance, especially at elevated temperatures, are required before ZrB_2 -ceramics can be used in thermal protection applications. Early stages of Adam's dissertation research centered on enhancing the densification and refining the microstructure of monolithic ZrB_2 and particulate-reinforced composites using commercially available raw materials and conventional hot pressing techniques. Improvements in processing provided moderate hot pressing temperatures (1900°C) and refined microstructures that improved the mechanical performance of the ZrB_2 ceramics. Additions of SiC provided further refinement in grain size and distribution that led to increased strength. ZrB_2 ceramics that contained SiC (20 or 30 vol%) particulates had room temperature flexure strengths that exceeded 1000 MPa, which is a significant improvement when compared to recent literature values of 600-700 MPa. This research was reported in the paper A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "High Strength ZrB_2 -Based Ceramics," *Journal of the American Ceramic Society*, 87(6) 1170-1172 (2004).

Analysis of the effects of oxide impurities and additives on densification led to the development of a pressureless sintering process for ZrB_2 . For the first time, monolithic ZrB_2 with high relative densities ($\sim 98\%$) was produced without the assistance of a liquid phase or external pressure. It was found that the addition of WC to ZrB_2 -SiC enabled densification by reacting with ZrO_2 that was present as an impurity. This research was reported in the paper A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Pressureless Sintering of Zirconium Diboride," *Journal of the American Ceramic Society*, 89(2) 450-456 (2006).

The primary objective of the final phase of the project is to utilize the knowledge gained from conventional hot pressing and pressureless sintering to develop reaction-based processes to produce UHTCs. During this stage, ZrB_2 and ZrB_2 -SiC will be formed using thermodynamically favorable reactions involving elemental zirconium and boron powders or other precursors. Successful production of these materials requires an understanding of the reaction sequence and the effect that powder processing has on reaction rates/temperatures and the final grain morphology. Examination of diffusion couples will provide further information about the reaction rates, activation energy, and diffusion directions during the reaction between elemental Zr and B. The results of this research will be reported in two forthcoming manuscripts dealing separately with ZrB_2 and ZrB_2 -SiC, respectively.

APPENDIX C. DISSERTATION OF JIM ZIMMERMANN

Jim Zimmermann has selected to complete his dissertation using the "publication" option available at UMR. His dissertation will consist of four submitted or published peer reviewed papers with an overall introduction, review of the relevant literature, an overall summary, and suggestions for future work. To date, none of the papers that will constitute Jim's dissertation have been submitted for publication. After approval by his dissertation committee, a copy of the entire dissertation will be available through the Curtis Laws Wilson Library at the University of Missouri-Rolla.

The manuscripts planned for Jim's dissertation are:

- 1) ZrB₂-SiC Ceramics Fabricated *In-Situ* by reactive hot pressing
- 2) Influence of Fabrication Methods on the Mechanical Properties of ZrB₂-25% SiC Ceramics
- 3) Thermal shock behavior of ZrB₂-30% SiC
- 4) Thermal shock behavior of ZrB₂-based fibrous monolithic ceramics

Manuscripts one and two will be based on Jim's work at ISTEC from October to December 2005. Manuscripts three and four will come from work completed at UMR. It is anticipated that all four manuscripts will be prepared and submitted during calendar year 2006.

APPENDIX D. PUBLICATIONS

Copies of the seven peer-reviewed publications that resulted from this project were provided to the program manager when the report was submitted. In addition, a copy of a paper that has been submitted for publication as well as a copy of the cover photograph for a special issue of the Journal of Materials Science were included.

List of Publications

1. W.G. Fahrenholtz, "Reactive Processing in Ceramic-Based Systems," International Journal of Applied Ceramic Technology, 3(1) 1-12 (2006).
2. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Pressureless Sintering of Zirconium Diboride," Journal of the American Ceramic Society, 89(2) 450-456 (2006).
3. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Oxidation of ZrB_2 -SiC Ceramics Under Atmospheric and Reentry Conditions," Refractories Applications Transactions, 1(2) 1-8 (2005).
4. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "High Strength ZrB_2 -Based Ceramics," Journal of the American Ceramic Society, 87(6) 1170-1172 (2004).
5. W.G. Fahrenholtz, G.E. Hilmas, A.L. Chamberlain, and J.W. Zimmermann, "Processing and Characterization of ZrB_2 -Based Monolithic and Fibrous Monolithic Ceramics," Journal of Materials Science, 39(19) 5951-5957 (2004). (UMR photo on cover of issue)
6. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Characterization of Zirconium Diboride Ceramics for Thermal Protection Systems," Key Engineering Materials, 264-268, 493-496 (2004).
7. A. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Characterization of Zirconium Diboride-Molybdenum Disilicide Ceramics," pp. 299-308 in Advances in Ceramic Matrix Composites IX, Ceramic Transactions, Volume 153, ed. by N.P. Bansal, J.P. Singh, W.M. Kriven, and H. Schneider, The American Ceramic Society, Westerville, OH (2003).

Cover Photograph

A copy of the cover of the Volume 39 Issue 19 of the Journal of Materials Science is included. The cover photograph was taken by for a press release at the University of Missouri-Rolla. It shows an oxy-acetylene torch heating a ZrB_2 ceramic to $\sim 2000^\circ\text{C}$.

Submitted Manuscript

1. W.G. Fahrenholtz, "Thermodynamic Analysis of ZrB_2 -SiC Oxidation: Formation of a SiC-Depleted Region," submitted to Journal of the American Ceramic Society, February 2006.